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Chemical interactions of thiophene with ZnO and Al-doped ZnO thin films

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ABSTRACT

In this study, ZnO and Al-doped ZnO films have been synthesized by five different deposition methods. Electrochemical measurements performed on films immersed in S-containing isooctane indicate that the texture and polarity of the surface of the films are key features affecting the adsorption of thiophene molecules. Specifically, ZnO films possessing a large amount of Zn-terminated (002) wurtzite surfaces are observed to be the most sensitive to the concentration of thiophene in isooctane.

1. Introduction

The objective of this study was to examine chemical reactions between ZnO and Al-doped ZnO films and concentrations of the aromatic sulfur species of thiophene (C_4H_4S) in isooctane. Although the interaction of ZnO with H_2S is well-studied [1], this research represents the first time that a combinatorial exploration was performed to investigate the effects that crystallinity, texture, and termination of ZnO and Al-doped ZnO thin films have on the adsorption of S-containing contaminants in a fluid. Since the fluid used in this study is isooctane, the results of this work are technologically relevant to the measurement of S content in diesel fuel, for example.

Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zincblende. Whereas the wurtzite structure is most stable at ambient conditions, deposition of ZnO on substrates with cubic lattice structures can stabilize the zincblende structure. The space group of the hexagonal structure is $P6_3mc$ (Hermann-Mauguin notation) or C_{6v}^4 (Schoenflies notation) with lattice constants of a = 3.25 Å and c = 5.2 Å. Wurtzite ZnO has a direct band gap of ~3.3 eV and is usually n-type in character, even in the absence of intentional doping. Controllable n-type doping is easily achieved by substituting Zn with group-III elements such as Al, or by substituting oxygen with group-VII elements such as chlorine or iodine.

ZnO is nearly insoluble in water and alcohol, but it reacts with gases like hydrogen sulfide according to.

$$ZnO + H_2S \rightarrow ZnS + H_2O \quad (1)$$

This reaction explains why ZnO powders are used commercially in products like deodorants, and why the magnitude of the change in resistivity with sulfur reaction probably depends upon the amount of surface area. Indeed, the ability to detect H_2S down to ppb levels at room temperature using sensors based on bundles of ZnO nanorods has been previously demonstrated [1].

Thiophene, benzothiophene, and dibenzothiophene can combine with ZnO to produce ZnS and furan, benzofuran, and dibenzofuran, respectively, according to the reactions:

$$\begin{aligned} ZnO + C_4H_4S &\rightarrow ZnS + C_4H_4O \\ ZnO + C_8H_6S &\rightarrow ZnS + C_8H_6O \\ ZnO + C_{12}H_8S &\rightarrow ZnS + C_{12}H_8O \end{aligned} \quad (2)$$

Many methods have been utilized to grow quasi-one dimensional (Q1D) metal oxide structures such as nanorods. According to the synthesis environment, they can be divided into two categories: vapor phase growth and liquid (solution) phase growth. Most of the metal oxide nanostructures are grown via the well-developed vapor phase technique, which is based on the reaction between metal vapor and oxygen gas.

MOCVD has been employed by many to synthesize ZnO-based Q1D arrays [2–10]. However, the SEM images shown in these publications do not indicate that the arrays form a structured thin film similar to

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that in Reference [1]. In a typical MOCVD process, liquid diethyl-zinc (DEZ) is placed in a temperature-controlled bubbler with Ar used as the carrier gas. DEZ, O_2, and N_2 combine on the heated substrate to form ZnO:N. To synthesize an Al-doped ZnO material, the N_2 source is replaced with a second temperature-controlled bubbler containing tetramethyl-aluminum (TMAl). In a slight modification of this process, a plasma source can be incorporated within the reactor to enhance the kinetics of the reactions and drive different film growth morphologies.

Chemical processes such as reverse micelle, sol–gel, aqueous solution and biomineralization methods have also been used to synthesize ZnO nanorods or nanowires [11–13]. Vayssieres described a template-less and surfactant-free aqueous approach to the growth of oriented ZnO nanorods that promises to enable large-scale and low-cost fabrication of these novel systems [13]. In this approach, glass substrates are immersed in an aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamine ($C_6H_{12}N_4$) at 95 °C for several hours, and then rinsed and dried. This process produces fairly well aligned, single crystal hexagonal nanorods with diameters of 100–200 nm and up to 10 μm long.

Reactive DC sputtering and RF magnetron sputtering are popular growth techniques for ZnO thin films. Compared to sol-gel and chemical-vapor deposition, magnetron sputtering is a preferred method because of its low cost, simplicity, and low operating temperature. ZnO films can be deposited at low substrate temperatures by RF sputtering of ZnO targets, and the deposition is usually carried out with $O_2/Ar + O_2$ ratios ranging from 0 to 1 and pressures between 10^{-3} and 10^{-2} Torr. O_2 serves as the reactive gas and Ar acts as the sputtering gas. DC sputtering of a Zn target in an $Ar + O_2$ gas mixture can also synthesize ZnO. ZnO films have been deposited by sputtering on different substrates including glass [14,15] and polymers [16]. In Ref. 16, ZnO:Al films were deposited onto various organic substrates in a RF magnetron-sputtering system. A sintered ceramic target with a mixture of ZnO and 3 wt% Al_2O_3 was used as source material. Processing variables included the target to substrate distance, the pressure of Ar, the sputtering power, and the substrate temperature. Under specific deposition conditions, c-axis textured wurtzite ZnO:Al films with good adhesion and low electrical resistivity were obtained.

This combinatorial study is comprised of the following elements. First, quantum chemical modeling of reactions between a thiophene molecule and the (002) surfaces of wurtzite ZnO was performed to address how thiophene adsorbs onto clean ZnO crystallographic surfaces. This modeling was performed to determine the sensitivity of the sulfur atom to the crystallographic surface site, and to calculate the energies necessary to rank the possible surface reactions. Next, ZnO and Al-doped ZnO films were deposited onto several substrate types and were characterized by X-ray diffraction and SEM. Finally, open circuit measurements were performed on thin films in isooctane standards containing quantified amounts of S.

2. Materials and methods

2.1. Reaction calculations

First principles calculations of reactions between a thiophene molecule and (002) surfaces of the wurtzite phase of ZnO were performed using the Gaussian 03 software suite of programs in an effort to illuminate possible reaction pathways [17]. Models were performed at the unrestricted Hartree Fock level using a 6-311G(d) basis set, which yielded good structural results with limited computing resources. The molecular orbital analyses were performed with the help of Gorelsky's AOMix program [18] and the Chemissian program [19].

Since the deposition of wurtzite ZnO films commonly results in (002) textured wurtzite films [20], the interaction of thiophene molecules with the (002) faces of the ZnO crystallographic structure was studied. The surface model in Fig. 1 is constructed as a $Zn_{24}O_{24}$ cluster such that the thiophene interaction occurs with fully coordinated surface atoms. The basis set for the C, H, and O atoms is Pople's 6-311G set [21], the basis set for Zn is the Los Alamos double zeta set, LANL2DZ [22]. These basis sets were found to yield acceptable relative energies in a reasonable computational time.

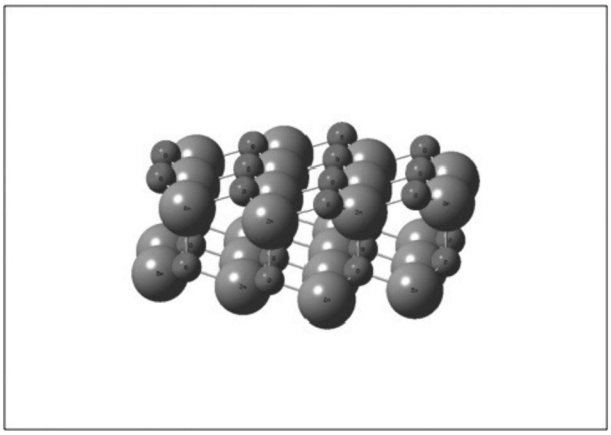

Fig. 1. O polar surface of the ZnO (002) surface. O atoms are the small red spheres, Zn atoms are the larger grey spheres. Size is proportional to the van der Waals radius. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Deposition of ZnO and Al-Doped ZnO

Thin films of ZnO and Al-doped ZnO (Al:ZnO) were deposited onto glass, silicon, and stainless steel substrates by vacuum- and solutions-based processes. Whereas the vacuum-based processes utilized were magnetron sputtering and metal organic chemical vapor deposition (MOCVD), the solutions-based processes were hydrothermal decomposition, anodization, and electrochemical deposition. All of these processes are known to have been successful in depositing ZnO films [23].

Two methods were used to deposit ZnO by hydrothermal deposition. In the method described by Xu et al. [24], a solution of 5 mM zinc-nitrate and 5 mM hexamethylenetetramine (HMTA) is mixed together in a 1:1 ratio. Substrates are immersed into the solution which is subsequently heated to 95 °C for durations between 4 and 48 h. In this study, it was observed that this method did not yield films with complete coverage on the substrates, the films were very thin, and tended to easily delaminate from the substrate surfaces.

In the second hydrothermal deposition method, $NH_4(OH)$ replaced HMTA, and the zinc-nitrate was dissolved in deionized water and heated to 70 °C, at which time $NH_4(OH)$ was added into the solution at 1 drop/s under continuous stirring until a white precipitate formed on the substrates. The precipitate was dehydrated at 95 °C for more than 3 h and then at 150 °C for an additional hour. This second method resulted in higher quality ZnO films on glass and silicon substrates as compared with the first method. The adhesion of the ZnO to the stainless steel was found to be extremely poor, much more so than in the case of the silicon substrates. Additionally, if the ZnO layer was too thick on the stainless steel substrate, the layer cracked and delaminated from the substrate.

Films grown with both hydrothermal deposition methods are very porous and do not form a homogeneous and strongly adherent layer on the substrate surface. As the films are immersed in liquids, ZnO particles become dislodged and float to the surface. Therefore, the hydrothermal processes used in this study were inadequate for the purpose of studying the adsorption of thiophene on ZnO.

Anodization is an electrolytic passivation process used to increase the thickness of the native oxide on metal surfaces. Anodized layers are grown by passing direct current through electrolytic solutions, with the metallic objects serving as the anodes (the positive electrode). The current releases hydrogen at the cathode (the negative electrode)

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