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Surface Science 600 (2006) 2972–2979
SURFACE SCIENCE
www.elsevier.com/locate/susc

Adsorption of 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane on ultra-thin CdS films

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Received 5 January 2006; accepted for publication 9 May 2006
Available online 2 June 2006

Abstract

The adsorption mechanism for the new compound, 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane (7ETTD), on ultra-thin films (~3 nm) of CdS is investigated. Multiple reflection absorption IR spectroscopy, in conjunction with inelastic electron tunneling spectroscopy, indicates that this compound forms a self-assembled monolayer adsorbed on the CdS surface via each molecule's trithia-adamantane anchor. Conductance–voltage data are recorded for tunnel junctions of the type Al/CdS/7ETTD/Pb over a temperature range of 4 K to room temperature and they indicate that the presence of the 7ETTD layer on the CdS dramatically modifies the conductance–voltage behavior of the junctions. These measurements show that different conduction mechanisms, including tunneling and possibly hopping, are responsible for charge transfer through the junctions depending on current, temperature, and voltage. WKB fits to the data are used to determine barrier parameters (height and width) for Al/CdS/Pb junctions with and without adsorbed 7ETTD layers on the CdS. Analysis of the fits shows that tunneling occurs at low bias (less than ~0.2 V) but, at higher bias voltages, modification of the barrier parameters alone is insufficient to account for the observed conductance changes. A frontier orbital model is invoked which does offer a plausible explanation for these conductance changes. The model assumes bias-dependent coupling between HOMO and LUMO states of the adsorbed 7ETTD and the surface states on the CdS. The present work suggests that, because of the marked effect on the conductance of CdS ultra-thin films, 7ETTD and other similar compounds may be candidates for use in molecular electronic device fabrication.

Keywords: Electron spectroscopy; Photovoltaics; Self-assembly; Sputtering; Cadmium sulfide; Tunneling; Amorphous thin films

1. Introduction

Electronic transport in organic semiconductor materials has gained increasing attention over the last thirty years [1]. Organic materials, in association with thin semiconductor films, can be used in a number of applications such as photovoltaic devices, solar cells, field-effect transistors, and other opto-electronic devices. Organic materials offer several advantages over conventional crystalline and amorphous inorganic semiconductor materials such as simplicity of deposition and the ability to tailor the band gap by changing chemical groups in the molecule. Also, substituting thin flexible films for brittle crystalline or amorphous materials opens up possibilities for low cost and versatile sources of energy conversion. Nevertheless, organic materials currently remain complimentary materials for semiconductor devices rather than competitive primarily due to poor efficiency and low charge mobility.

A great variety of organic molecules have been identified that can be used as self-assembled-monolayers (SAMs). Some of them contain carboxylate groups [2–4] which, because of their polar nature, enhances conditions for self-assembly [5]. Others contain active sites with atoms like sulfur and selenium which may rely on physisorbtion and a strong affinity to the atoms of the surface for arrangement [6]. One of the promising categories of SAMs is a new family of compounds based on a trithia-admantane anchor

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doi:10.1016/j.susc.2006.05.011

developed by Hu [7,8]. In these compounds, three sulfur atoms are conveniently sitting at the end of a tripod which allows the molecules to adsorb on various surfaces including gold.

CdS, along with CdSe and CdTe, are viable semiconductor materials for thin-films photovoltaic devices and have band gaps in the range 1.4–1.5 eV. These materials can be used also for the fabrication of hybrid heterojunctions. The presence of organic layers in heterojunctions tends to improve surface smoothness and the layers can also be used for light conversion [9]. But the problem of the contact resistance between semiconductors layer and metal electrode and trapping levels remains [10,11].

In the present work we present data on the adsorption of the new compound 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}] decane (7ETTD) (Fig. 1) on an ultra-thin film of CdS. We will show that the compound adsorbs on the semiconductor surface by orienting in the right arrangement to form a heterojunction and we will investigate the electronic properties of these heterojunctions. Their current–voltage dependences are recorded over a temperature range of 4.2–300 K, and temperature dependent conductance–voltage $G(V,T)$ data derived from those measurements allow us to determine the associated conductance mechanisms in the heterojunctions. Inelastic electron tunneling spectroscopy (IETS) is also used to characterize the electronic properties of the junctions. IETS has been shown to be a useful tool for investigating physical phenomena on surfaces. IETS was discovered around 40 years ago by Jaklevic and Lambe [12], and there have been several extensive reviews of the technique since then. Three of the most informative works on IETS are probably the authoritative book on the subject edited by Hansma [13], a thorough review article by Brown [14] and an up-to-date review article by Hipps and Mazur [15] which incorporates recent developments. The reader is directed to these sources, and references therein, for a full description of the technique. The present workers have used IETS previously to study vibrational spectra of ultra-thin sputtered films of germanium oxide, silicon and its oxides and also CdTe oxides [16–18]. IETS has an advantage over IR and Raman spectroscopy since the signal-to-noise ratio increases for thinner film, such as those under investigation in the present work. IETS has also been shown to be a convenient technique for investigating tunnel barrier parameters for thin layers of semiconductors [15] and this aspect is extended to the present CdS systems under investigation.

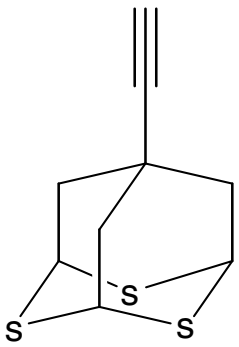

Fig. 1. Structural model of 7-ethynyl-2,4,9-trithia-tricyclo[3.3.1.1^{3,7}]decane (7ETTD).

2. Experimental method

2.1. Tunnel junction fabrication

Al/barrier/Pb tunnel junctions were fabricated using standard vacuum deposition techniques. The Al and Pb films were evaporated from resistively heated sources, and CdS barrier layers were formed by RF sputtering as described below.

A stainless steel vacuum chamber with a base pressure 10^{-6} Torr was used for preparation of the tunnel junctions. Prior to each junction fabrication the chamber was cleaned in an oxygen and argon plasma discharge, and the RF sputter gun was cleaned with argon. Next the Al electrodes were evaporated onto a glass substrate. Depending on the required barrier, one or more of the following procedures were adopted:

(a) The sample was removed from the chamber and spin doped with solvent (dichloromethane or diethylether). This procedure was employed to prepare control samples to ensure that there is no contamination in the chamber or solvent.
(b) RF sputtering of CdS in a background of argon with chamber pressure ~50 mTorr. A 2 in. diameter 0.25 in. thick 99.999% pure CdS sputter target, supplied by Kurt J. Lesker Company, was used. Deposition rates were in the range 0.01–0.02 nm/s. The thickness of CdS films was 3 nm determined by a quartz film thickness monitor.
(c) First, a CdS film was sputtered as described in (b), then the film was spin doped with (7ETTD) dissolved in dichloromethane and diethylether in the following proportion: 9 mg 7ETTD/2 ml dichloromethane/13 ml diethylether. Such a solution was found to produce more uniform surface coverage of the adsorbate as indicated by corresponding tunnel junction resistance measurements.

To complete the fabrication process, tunnel junctions were capped with an approximately 300 nm thick lead cover-electrode. We used 99.999% pure or better source materials for both Al and Pb. Fig. 2 shows a schematic diagram of the sample.

2.2. I–V and conductance–voltage (G–V) measurements

Four terminal I–V measurements were performed, and the data were recorded using a commercially available data acquisition software package. Conductance–voltage (G–V) data were derived numerically from I–V measurements, by