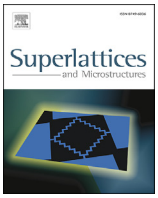
Superlattices and Microstructures 97 (2016) 378–385

Contents lists available at ScienceDirect

Superlattices and Microstructures

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



Improved microstructure and performance of PbS thin films via *in-situ* thermal decomposition of lead xanthate precursors using self-assembling monolayer

Jingni Wang [a], [1], Kai Yao [b], [1], Zhenrong Jia [a], Xiaofeng Wang [a], Fan Li [a], *

[a] Department of Materials Science and Engineering, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China
[b] Institute of Photovoltaics, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

ARTICLE INFO

Article history:
Received 18 June 2016
Accepted 24 June 2016
Available online 2 July 2016

Keywords:
PbS thin film
Lead xanthate precursors
Thermal decomposition
Self-assembling monolayer
Photoelectric response

ABSTRACT

Microstructure control is critical to achieve thin film-based devices with high performance. The surface properties of the substrates on which thin films grow are expected to greatly influence the morphology and the resulting performance. Generally, homogeneous, dense and highly crystalline films are required. However, “island” like structures are usually obtained mainly due to the non-uniform nucleation. In this article, the self-assembling monolayer (SAM) strategy was applied to efficiently realize the uniform nucleation and modulate the microstructure of lead sulfide (PbS) thin films, which were fabricated on the modified ZnO-coated substrates with 3-mercaptopropionic acid (MPA) SAM via *in-situ* thermal decomposition of lead xanthate precursors. The results showed that PbS thin films with reduced pin-holes and uniform crystalline grains were fabricated with the incorporation of MPA SAM. More importantly, PbS thin films modulated by MPA showed better photoelectric response.

1. Introduction

In recent years, with the development of material science, semiconductor thin film technology has been developed rapidly and semiconductor thin films have been widely used in many fields due to their unique properties and excellent performance. Lead sulfide (PbS), an important IV-VI group p-type semiconductor, has a narrow direct bandgap (0.41 eV at 300 K), high absorption coefficient of ~10^5 cm^{-1} in visible light [1,2] and large excitation Bohr radius (18 nm) [3], which has been applied in photoconductive IR detectors, electroluminescent devices, solar cells, multiple exciton generation, and so on [4–6].

At present, there are several techniques to fabricate PbS thin films, such as chemical bath deposition, chemical vapor deposition, spin-coating, spray pyrolysis, successive ionic layer adsorption and reaction (SILAR) and thermal decomposition [7–11]. Among numerous techniques, thermal decomposition of metal xanthate precursors is proved to be a convenient, easily-manipulated, low-cost, highly efficient route to fabricate nanostructured metal sulfide thin films [12–14]. Generally, homogeneous, dense and highly crystalline films are required. However, three-dimensional “island”-like structures with poor crystallinity were usually obtained, mainly due to the non-uniform nucleation owing to the complex crystal growth

---

* Corresponding author.
E-mail address: lfan@ncu.edu.cn (F. Li).

[1] These authors contribute equally to this work.

http://dx.doi.org/10.1016/j.spmi.2016.06.041
0749-6036/© 2016 Elsevier Ltd. All rights reserved.

process during the thermal decomposition of lead xanthate precursors, leading to negative influence on the device performance.

To improve the microstructure of PbS thin films, a great deal of research efforts have been devoted, such as delicate control of ligand exchange of precursors, concentration of precursors, annealing temperature and time, etc. [15–19] Meanwhile, it has been reported that ligands play crucial roles in determining the morphology, optical and electric properties of PbS thin films and many kinds of ligands have been reported, such as benzenedithiol [20], ethanedithiol [21], thiocyanate [22] and et al. Besides, PbS thin films are usually prepared on substrates during the device fabrication, therefore, the surface properties of substrates are expected to greatly affect the nucleation and crystallization of PbS and, thus, the resulting microstructure of PbS thin films. As we know, in general, good wetting property between substrates and thin films favors achieving homogeneous crystalline structure [23]. Based on the above analysis, modification of substrates with self-assembling monolayers (SAM) composed of ligands containing two anchoring groups, one of which are bonded onto the substrates and the other of which can bond with the thin films, not only can improve the wetting property, but also can promote the uniform nucleation, directing the crystalline evolution and achieving the improved microstructure [24,25]. However, this topic is rarely explored for PbS thin films.

In this work, as a facile and efficient approach, SAM strategy was applied to solve the non-uniform nucleation over large-scale substrates and to modulate the microstructure of PbS thin films for performance improvement. Lead sulfide (PbS) thin films, which were prepared on the ZnO-coated substrates modified with 3-mercaptopropionic acid (MPA) acting as SAM via *in-situ* thermal decomposition of lead xanthate precursors, were chosen to investigate the modulating effect of SAM on film homogenization and microstructure associated with crystalline structure, coverage, optical absorption, and photoelectric response.

2. Experimental section

2.1. Materials

All reagents, lead acetate ($Pb(CH_3COO)_2{\cdot}3H_2O$, 99.99%), potassium ethyl xanthate ($C_3H_5KOS_2$, 98%), pyridine (C_5H_5N, $\geq$99.9%), 3-mercaptopropionic acid ($C_3H_6O_2S$, MPA, 98%), methyl alcohol (CH_3OH, AR 99.5%), zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99.9%) and N,N-dimethylformamide (DMF, 98%) were purchased from Aladdin. Ethanolamine ($NH_2CH_2CH_2OH$, 99.5%) and 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 99.8%) were purchased from Aldrich. Dichloromethane (CH_2Cl_2) and acetone were of analytical grade. Indium-tin-oxide-coated glass (ITO/glass), with a sheet resistance of ~15 Ω sq^{-1}, was cut into 15 × 15 mm^2 and used as substrates.

2.2. Cleaning of glass/ITO

The glass/ITO substrates were ultrasonically washed in detergent water, deionized water, acetone and isopropyl alcohol for 20 min, respectively. And then the substrates dried under a stream of nitrogen flow.

2.3. Preparation of ZnO layers on glass/ITO substrates

The ZnO layers on glass/ITO substrates were prepared through an in-situ sol-gel process according to literature methods [26]. Firstly, the ZnO precursor was prepared by dissolving 1 g zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) in 10 mL 2-methoxyethanol ($CH_3OCH_2CH_2OH$). 0.28 mL ethanolamine ($NH_2CH_2CH_2OH$) was added to stabilize the precursor before vigorous stirring for 12 h for the hydrolysis reaction in air. Subsequently, the ZnO precursor was spin-coated on top of the glass/ITO substrates, which were cleaned with oxygen plasma to remove organic residues prior to spin-coating, for a thickness of approximately 50 nm. Before they were completely dry, those films were immediately placed onto a hot plate at room temperature. Then the films were heated until the temperature reached 200 °C at a ramping rate of 50 °C/min, and one more hour was needed to anneal samples further. The substrates were subsequently removed from the hot plate to cool down.

2.4. Preparation of lead xanthate precursors-$Pb(S_2COEt)_2(C_5H_4N)_2$

$Pb(S_2COEt)_2(C_5H_4N)_2$ was fabricated according to the literature [27,28]. In brief, an aqueous solution of potassium ethyl xanthate was added to a rapidly stirring aqueous solution of lead acetate in a molar ratio of 2:1. The precipitate was filtered and washed with water followed by methanol, and then dried at 40 °C in a vacuum oven. Then the dried precipitate was dissolved in dichloromethane/pyridine solution and the molar ratio of precipitate and pyridine is 1:2, and then stirred for 30 min at room temperature. The excess solvent was removed by rotary evaporation and $Pb(S_2COEt)_2(C_5H_4N)_2$ was obtained as white powder. Finally, the raw product was dissolved in acetone at 50 °C and recrystallized at 4 °C for three times.