



Iron selenide films by aerosol assisted chemical vapor deposition from single source organometallic precursor in the presence of surfactants



Raja Azadar Hussain^a, Amin Badshah^{a,*}, Adnan Younis^b, Malik Dilshad Khan^a, Javeed Akhtar^c

^a Department of Chemistry, Quaid-i-Azam University, 45320 Islamabad, Pakistan

^b School of Materials Science and Engineering, University of New South Wales, Sydney 2052, NSW, Australia

^c Department of Physics, COMSATS Institute of Information Technology, Park Road, Chak Shahzad, Islamabad, Pakistan

ARTICLE INFO

Article history:

Received 13 January 2014

Received in revised form 23 July 2014

Accepted 24 July 2014

Available online 6 August 2014

Keywords:

Iron selenide

Aerosol assisted chemical vapor deposition

Ferrocene

Selenourea

Scanning electron microscopy

ABSTRACT

This article presents the synthesis and characterization (multinuclear nuclear magnetic resonance, Fourier transform infrared spectroscopy, carbon–hydrogen–nitrogen–sulfur analyzer, atomic absorption spectrometry and thermogravimetric analysis) of a single source organometallic precursor namely 1-acetyl-3-(4-ferrocenylphenyl) selenourea for the fabrication of iron selenide (FeSe) films on glass substrates using aerosol assisted chemical vapor deposition (AACVD). The changes in the morphologies of the films have been monitored by the use of two different surfactants i.e. triton X-100 and tetraoctylphosphonium bromide during AACVD. The role of surfactant has been evaluated by examining the interaction of the surfactants with the precursor by using UV–vis spectroscopy and cyclic voltammetry. The fabricated FeSe films have been characterized with powder X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the recent years FeSe has been synthesized with electrodeposition [1,2], pulsed laser deposition [3,4], chemical vapor deposition [5–8], chemical vapor transport [9], chemical bath deposition [10,11], spray pyrolysis [12], molecular beam epitaxial growth [13], solid state reaction [14], solid state reaction at different sintering temperatures [15], thick films from high temperature solution [16] and rapid, solvent-less reaction under autogenic pressure at elevated temperature [17]. Different physical parameters and applications such as photoemission spectrum [18], band structure, magnetic behavior, electronic structure, phonon spectrum, superconductivity, Mossbauer, and Raman and X-ray diffraction (XRD) spectra have now been established.

The use of surfactants in liquid phase affects the particle size, orientation, morphology, mechanical strength, corrosion properties, luminescent properties and photoelectric properties of the deposited materials [19–21]. But the effect of surfactants on gas phase reactions has not been investigated. In our previous publications [22–24] we have discussed in detail the synthesis and biological applications of ferrocene incorporated selenoureas (FIS) but this article deals with the synthesis of a FIS namely 1-acetyl-3-(4-ferrocenylphenyl)selenourea (PA) with characterization (multinuclear nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), carbon–hydrogen–nitrogen–sulfur analyzer (CHNS), atomic absorption spectrometry

(AAS) and thermogravimetric analysis (TGA)) and its conversion to FeSe films with the help of aerosol assisted chemical vapor deposition (AACVD) under the influence of different concentrations of two different surfactants i.e. triton X-100 (triton) and tetraoctylphosphonium bromide (TOPBr). The basic idea in mind was that the temperature range in which our FIS starts decomposing is lower than the boiling points of both the surfactants used i.e. when thermal decomposition of precursor is in progress then the surfactants are available in the reaction atmosphere in the liquid or vapor state. So we have investigated the surfactants' effect (at three different concentrations) on the morphologies of the fabricated FeSe films with respect to that film in which surfactants were not employed. Even before the start of thermal decomposition i.e. during the formation of aerosol, surfactants will show the effect of their presence.

2. Experimental details

2.1. Materials and methods

Melting point was determined in a capillary tube using Gallenkamp (U.K.) electrothermal melting point apparatus. Infrared spectrum was taken on Thermoscientific NICOLET 6700 FTIR between 4000 and 400 cm^{-1} . ^1H and ^{13}C NMR spectra were recorded between 0–13 ppm and 0–210 ppm respectively on Jeol JNM-LA 500 FT-NMR. $\text{Si}(\text{CH}_3)_4$ was used as an internal reference. The elemental analysis was performed using a LECO-932 CHNS analyzer while the Fe concentrations by AAS were determined on an Atomic Absorption Spectrophotometer

* Corresponding author.

E-mail address: aminbadshah@yahoo.com (A. Badshah).

Perkin Elmer 2380. FeSe thin films were characterized with CuK α radiation of 0.154 nm between diffraction angles 10 and 80. SEM (scanning electron microscopy) images were taken on a SEM JEOL model, 5910 LV with an accelerating voltage of 20 kV at high vacuum mode and secondary electron image. The semi-quantification elemental analysis to find out the weight percentage of the elements was carried out by using OXFORD INCA energy dispersive X-ray spectrometer 7274 (EDS). Absorption spectra were recorded on Shimadzu 1800 spectrophotometer. First the spectrum of 20 μ M free PA dissolved in ethanol was run with 0.2 mL of solvent and then with 0.2 mL of triton and TOPBr separately to note the change of absorption.

Cyclic voltammetry (CV) was performed on Biologic SP-300 cyclic voltammeter running with EC-Lab Express V 5.40 software, Japan. Before every reading working electrode was polished with alumina powder and rinsed with distilled water. Analytical grade KCl was used as supporting electrolyte and nitrogen gas (99.9%) was purged through the mixture to avoid interference of oxygen. CV behavior was evaluated with a setup having three electrode system i.e. working (platinum disc electrode) reference (Ag/AgCl) and auxiliary electrodes (platinum wire electrode). Changes in peak potentials were monitored to have information about the mode of interaction and decrease in peak current gave information about the PA–Triton adduct. Values of diffusion coefficients were determined by the following form of Randles–Sevcik equation [23–25]:

$$I_{pa} = 2.69 \times 10^5 n^{3/2} A C_0^* D_0^{1/2} \nu^{1/2} \quad (1)$$

where I_{pa} is the anodic peak current, C_0^* is the reductant's concentration in mol cm^{-3} , A is the geometric area of the electrode in cm^2 , n is the number of electrons involved in the process, and D_0 is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$ [22–24].

Ferrocene, paranitro aniline, sodium nitrite, diethyl ether, acetone, dimethyl sulfoxide (DMSO), Pd-charcoal, acetyl chlorides and hydrazine were purchased from Sigma Aldrich. Paraferrocenylaniline was synthesized by a procedure reported by our group previously [26].

For electrical properties of FeSe a representative film was coated on ITO (indium tin oxide) conducting glass by AACVD using PA. Electrical conductivity of this film was determined by the two probe DC conductivity method between the temperature ranges of 298.15 K and 389.15 K by Digital Multimeter Model DMM 2001, Laboratory Power supply

30 V/5A, Laboratory Oven. For the measurement of electrical resistivity the following formula was used:

$$\rho = R \cdot A/L$$

where ρ is electrical resistivity, R is electrical resistance, A is cross sectional area in cm^2 and L is length in cm.

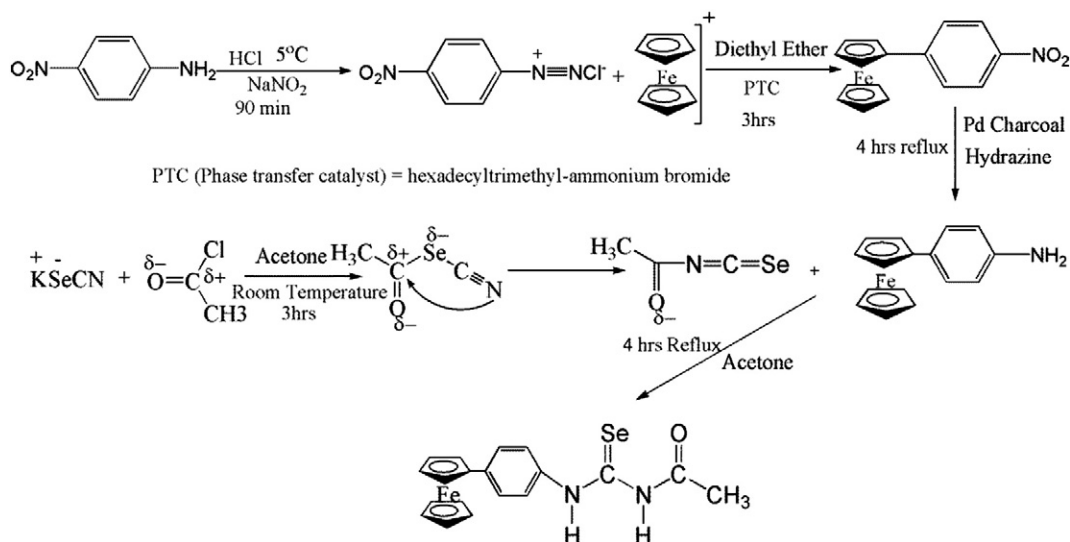
2.2. Synthesis and fabrication

2.2.1. 1-Acetyl-3-(4-ferrocenylphenyl)selenourea (PA)

PA was synthesized by the reaction of isoselenocyanate with 4-ferrocenylaniline in a one pot procedure using dried acetone as a solvent inside a two necked round bottom flask. Isoselenocyanate was synthesized in the first step by reacting 0.7 g (0.005 mol) of potassium selenocyanate (KSeCN) with 0.35 mL (0.005 mol) of acetyl chloride [22–24] under constant magnetic stirring for 4 h at room temperature. The resulting yellow colored product with a suspension of potassium chloride was then mixed with 1.38 g (0.005 g) of 4-ferrocenylaniline in the second step and the reaction mixture was stirred under reflux for a further 4 h. The progress of the reaction was monitored with the help of thin layer chromatography. Orange colored product obtained in the solution state was mixed with cold water to remove the impurities and have the product in solid state, which was washed with n-hexane and recrystallized in acetone with 73% yield (Scheme 1). Decomposition temperature 139 °C; elemental analysis % Calc. (found): carbon 53.64 (53.39), nitrogen 6.50 (6.38), hydrogen 4.23 (4.19), Fe 13.17 (13.15); ^1H NMR (benzene): δ (ppm) 13.01 (s, 1H), 10.70 (s, 1H), 8.1–7.3 (m, 4H), 4.80 (t, 2H), 4.37 (t, 2H), 4.11 (s, 5H), 2.98 (s, 3H); ^{13}C NMR (benzene): δ (ppm) 179.0 (1C), 165.3 (1C), 136.4 (1C), 135.6 (1C), 129.3 (2C), 128.7 (2C), 84.6 (1C), 69.5 (5C), 69.4 (2C), 66.3 (2C), 23.1 (1C); FT-IR: 3400–3100 (b), 2956, 1659, 1605, 1585, 1542, 1258, 1153.

2.3. Fabrication of FeSe films by AACVD

FeSe thin films were deposited using AACVD kit equipped with CARBOLITE furnace (21-101847, type MTS10/15/130) and Deurer living LB44 humidifier, having ultrasonic system on glass substrates. Optimized concentrations of PA (0.08 g) were dissolved in 15 mL of toluene in a two necked round bottom flask (100 mL) equipped with a glass inlet. This inlet was attached to one of the necks (of two necked round



Scheme 1. Synthesis of 1-acetyl-3-(4-ferrocenylphenyl)selenourea.

Download English Version:

<https://daneshyari.com/en/article/1665325>

Download Persian Version:

<https://daneshyari.com/article/1665325>

[Daneshyari.com](https://daneshyari.com)