



Formation of inorganic nanocomposites by filling TiO₂ nanopores with indium and antimony sulfide precursor aerosols



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ABSTRACT

Nanocomposites of nanoporous-TiO₂/In₂S₃ and np-TiO₂/Sb₂S₃ were formed by deposition of In₂S₃ or Sb₂S₃ using spray ion layer gas reaction technique from their precursor solutions onto nanoporous TiO₂ substrates at temperatures of 150, 175 and 200 °C. The least penetration of the precursor into np-TiO₂ was achieved for np-TiO₂/In₂S₃ nanocomposites from indium acetylacetonate salt. The deepest penetration was obtained for both np-TiO₂/In₂S₃(Cl) and np-TiO₂/Sb₂S₃ nanocomposites with effective diffusion coefficients of $3.3 \times 10^{-3} \text{ cm}^2/\text{s}$ and $3.2 \times 10^{-3} \text{ cm}^2/\text{s}$, respectively. The transport of the precursors in np-TiO₂ and the formation of different nanocomposites were described the regime of the Knudsen diffusion model.

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1. Introduction

Nanocomposites are formed when two different materials are mixed on a nanometer scale to produce a new material with new properties [1]. The intrinsic material properties and interface and size effects of inorganic nanocomposites make them suitable materials for various device applications. The formation of inorganic nanocomposites may involve deposition of an inorganic semiconductor material into a nanostructured/porous substrate. The porous substrates allow for the formation of nanocomposite layers by deposition of semiconductor materials from gaseous precursors.

Preparation of nanocomposites involves the transport and deposition/reaction of the gaseous precursor species through the nanopores. The transport mechanism, and hence filling of the nanopores, depends on the size of the pores, concentration of the gaseous precursor diffusing in the nanoporous substrate, size and shape of the diffusing molecules, pressure and deposition temperature affecting both diffusion and pyrolysis reaction rates [2]. Depending on the pore size, different mechanisms will dominate pore transport [3]. The mean free path of diatomic inorganic gases is on the order of 10^3 Å [4]. If the mean free path of the diffusing species is smaller or larger than the diameter of the pore, then the molecular transport in the pores proceeds by bulk or Knudsen

diffusion mechanism, respectively. The Knudsen diffusion is known to dominate for pores with diameters ranging from 10 to 10,000 Å [4]. The dominant pore transport process can be determined by the Knudsen number, which is the ratio between the mean free path and pore diameter. For pores with diameters between 3 and 10 Å, surface diffusion dominates, while activated diffusion, also called molecular sieving dominates when the pore diameter is less than 3 Å [3,5,6].

The Knudsen diffusion coefficient (D_K) analyzed according to the kinetic theory of gases is given by Eq. (1) [4,7] assuming a cylindrical pore geometry,

$$D_K = \frac{2}{3} \cdot \bar{r} \cdot \bar{v} = 9.7 \times 10^3 \cdot \bar{r} \cdot \sqrt{\frac{T}{M}} \quad (1)$$

where \bar{r} is the average pore radius, \bar{v} is the average molecular velocity, T is the temperature in Kelvin scale and M is the molecular mass. D_K is proportional to the pore radius \bar{r} . Numerical values of D_K for diatomic gases range from 0.01 cm²/s for pore radius of 10 Å to 10 cm²/s for pore radius of 10,000 Å [4]. The pore transport of the gaseous species is accompanied by simultaneous deposition on the internal walls of the pores. For example, a highly diffusive species will penetrate deeper in the porous matrix, while a species with a high deposition rate will close the pores faster and limit the penetration depth due to preferential deposition and narrowing of the pore diameter near the surface [8]. These depend on the substrate properties and precursor characteristics [2].

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Several methods have been used to deposit semiconductor materials onto porous substrates including chemical vapor deposition (CVD) [9, 10], electrochemical vapor deposition (EVD) [11,12], atomic layer epitaxy (ALE) [13], spray pyrolysis [14], successive ionic layer adsorption and reaction (SILAR) [1], atomic layer deposition (ALD) [2], plasma sputtering [15] and ion layer gas reaction (ILGAR) [16,17]. ILGAR is a sequential and cyclic deposition technique suitable for the deposition of conformal thin films on different types of substrates [17,18]. ILGAR has proved to be suitable for coating nanorods with In_2S_3 thin films up to more than $3\ \mu\text{m}$ long [19] and up to $10\ \mu\text{m}$ long on metallic nanorods [20]. Deposition of various substrates is possible with different precursor salts, concentrations and deposition temperatures above a threshold.

In this work, we report the application of ILGAR for the formation of nanocomposites by deposition of different indium and antimony sulfides onto nanoporous TiO_2 substrates. The penetration of the gaseous precursor and pore closure was investigated by depth profiling the In and Sb precursors in the nanoporous scaffold using the Rutherford backscattering spectrometry (RBS). RBS as an absolute method is suitable for compositional and depth profiling analysis in planar and structured samples [2,15].

2. Experiments

The nanoporous TiO_2 substrates were prepared by screen printing of a commercial paste containing TiO_2 nanoparticles of 25 nm diameter onto a $\text{SnO}_2:\text{F}$ (FTO) coated glass. The substrates were then sintered at $520\ ^\circ\text{C}$ for 30 min [16]. The inorganic nanocomposites were formed by deposition of In_2S_3 onto the nanoporous TiO_2 by ILGAR technique from InCl_3 or $\text{In}(\text{acac})_3$ precursor salt dissolved in ethanol [17,18]. The corresponding nanocomposites are hereby termed $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ or $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$, respectively. Two concentrations of the precursor solutions of 25 and 15 mM were used. In another set of samples, Sb_2S_3 was deposited on np-TiO_2 substrates by ILGAR from a 25 mM precursor solution of SbCl_3 in ethanol to form $\text{np-TiO}_2/\text{Sb}_2\text{S}_3$ nanocomposites. Up to 12 ILGAR cycles of In_2S_3 and of Sb_2S_3 were deposited onto the np-TiO_2 substrates at temperatures of 150, 175 and $200\ ^\circ\text{C}$. The penetration of In_2S_3 or Sb_2S_3 inside the nanoporous TiO_2 scaffold was investigated by depth profiling with RBS. RBS experiments were performed using 3MV Tandemron accelerator equipped with a beam line for ion beam analysis and sample manipulation mechanism with four axes goniometers. An incident ion beam of He^+ of 1.44 MeV was used and the backscattered ions were detected at a scattering angle of 170° .

3. Depth profiling

Fig. 1 shows RBS spectra from $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$, $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ and $\text{np-TiO}_2/\text{Sb}_2\text{S}_3$ nanocomposites for In_2S_3 and Sb_2S_3 deposited at $200\ ^\circ\text{C}$ from 25 and from 15 mM precursor solutions. The elements detected from the nanocomposites are indicated, with the heavier atoms appearing at higher channel numbers and lighter elements at lower channel numbers. The high In signals from the surface of both $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ and $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ nanocomposites show the presence of a capping layer on top of np-TiO_2 . $\text{np-TiO}_2/\text{Sb}_2\text{S}_3(\text{Cl})$ nanocomposite did not have a capping layer independent of precursor concentration and deposition temperature.

The In signal from the $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ surface depicts a thicker capping layer compared to $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ for both precursor concentrations. The height of the In signal from $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ was larger for $\text{In}_2\text{S}_3(\text{Cl})$ deposited from 25 mM compared to 15 mM precursor solutions. For $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ nanocomposite, the width of the In signal decreased with a reduction in the precursor concentration. The degree of precursor penetration and deposition in the porous substrate depends very much on the characteristics of the precursors such as diffusivity and deposition rates.

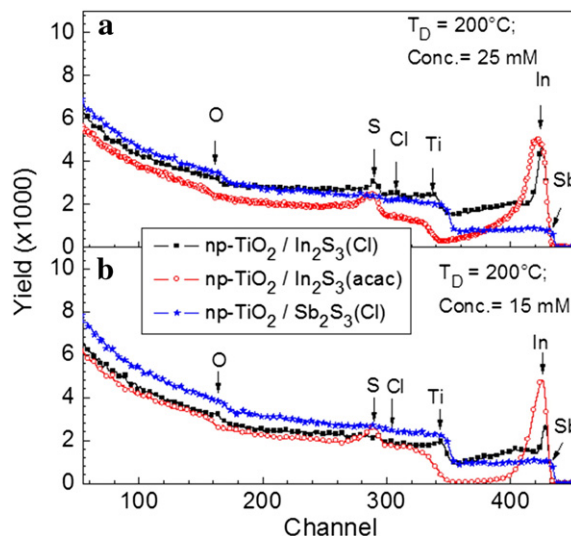


Fig. 1. RBS spectra for $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ (squares), $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ (circles) and $\text{np-TiO}_2/\text{Sb}_2\text{S}_3(\text{Cl})$ (triangles) nanocomposites prepared at $200\ ^\circ\text{C}$ from (a) 25 mM and (b) 15 mM precursor solutions.

The tails on the In or Sb signals observed in Fig. 1 denote concentration gradients concomitant with the penetration of the InCl_3 or SbCl_3 gaseous precursors into the pores of np-TiO_2 , respectively. The RBS signals from Ti, S, Cl and O overlap strongly with each other and cannot therefore be used reliably to investigate the formation of the nanocomposites. Depth profiling of the In and Sb elements was used to compare the quality of penetration and the formation of a capping layer by the deposited In_2S_3 and Sb_2S_3 , respectively, which describe the extent of penetration by the respective precursor. The In and Sb signals are fairly separated and only overlap at the lower channel numbers with the Ti signals.

Fig. 2 shows the depth profiles of In from $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ and $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ deposited at temperatures of 200 and $175\ ^\circ\text{C}$ from 25 and from 15 mM precursor solutions. The depth profiles were obtained using the Nuno's Data-Furnace (NDF) code [21]. In Fig. 2(a), the depth profiles are compared for both nanocomposites prepared from 25 mM

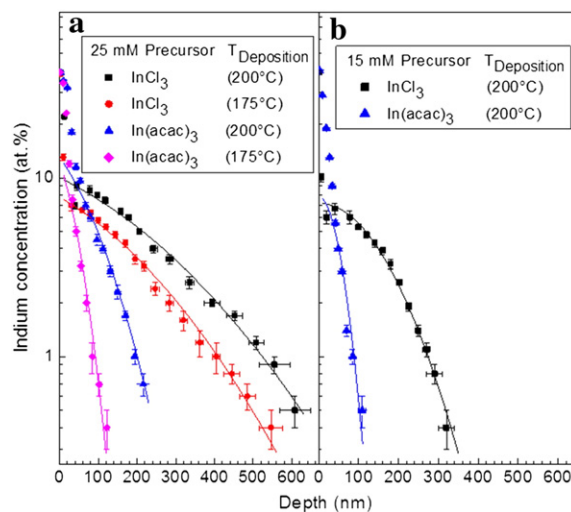


Fig. 2. Depth profiles of indium concentration from $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{Cl})$ and $\text{np-TiO}_2/\text{In}_2\text{S}_3(\text{acac})$ nanocomposites after deposition from precursor concentrations of (a) 25 and (b) 15 mM at 200 and $175\ ^\circ\text{C}$ temperatures.

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