

Template assisted synthesis of nanoscale layers of lead selenide and lead telluride

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Abstract

Thin layers of lead selenide or lead telluride nanoparticles were synthesized by spincoating solutions of polyethyleneoxide (PEO) and a single-source-precursor for either PbSe or PbTe on a silicon substrate. Subsequently the precursors were converted to the lead chalcogenide by thermolysis and the polymer was thermally removed. $\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ ¹ and $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$ ² were used as organometallic single-source-precursors yielding very pure crystalline lead selenide and lead telluride via thermolysis in inert gas atmosphere at temperatures above 400 °C or 250 °C, respectively. This template-based method can be regarded as a first step towards multilayered superstructures of PbSe and PbTe or ternary phases. Furthermore it represents a very simple one step approach to lower dimensional thermoelectric materials which can easily be transferred to other systems when molecular precursors are available.

Introduction

Lead selenide and lead telluride are known as small band gap semiconductor compounds. They both display a high ZT in the bulk, lead telluride even represents one of the most efficient thermoelectrics in the temperature range from 400 to 500 °C. Even higher ZTs could already be realized by the synthesis of nano-layered superstructures in the PbSeTe/PbTe system via molecular beam epitaxy (MBE)³ or evaporation methods⁴. By chemical vapour transport (CVT) methods high-quality lead chalcogenide (S, Se, Te) nanowires were fabricated and also characterized regarding

their thermoelectric behaviour⁵. Template-based methods also present a promising approach towards the synthesis of lower dimensional functional materials such as polymer fibers or semiconductor and noble metal layers or nanowires. In this work polymer films produced by spincoating were used as templates for the synthesis of nanoscale layers of PbSe and PbTe films starting from organometallic single-source precursors finely dispersed in the polymer matrix.

Results and Discussion

$\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ and $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$ were synthesized according to literature methods^{1,2} and their thermal decomposition was monitored using Thermogravimetric Analysis (TGA). As matrix for the thermal decomposition of the precursors to PbSe and PbTe, a polymer had to be found which represents on the one hand a stable matrix in the temperature range of the precursors' decomposition but which can on the other hand be completely removed by thermolysis at higher temperatures. PEO with an average molar weight of 900.000 g/mol was chosen as it displays a thermal degradability of 100% and because very homogeneous films with a thickness of 100 to 300 nm could be prepared by spincoating solutions of PEO and the precursors onto silicon or glass substrates. The TGA revealed that PEO degrades completely at temperatures of about 425 °C (Fig. 1). The thermal degradation of $\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ (Fig.2) already takes place in the range from 180 °C to 275 °C whereas $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$ is decomposing from 150 °C to 250 °C. These results show

that a formation of PbSe and PbTe particles in an intact polymer matrix of PEO can be expected.

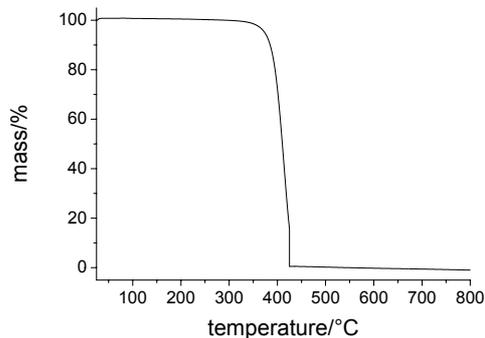


Figure 1. TG decomposition profile of PEO in a nitrogen atmosphere at a heating rate of 7 °C/min.

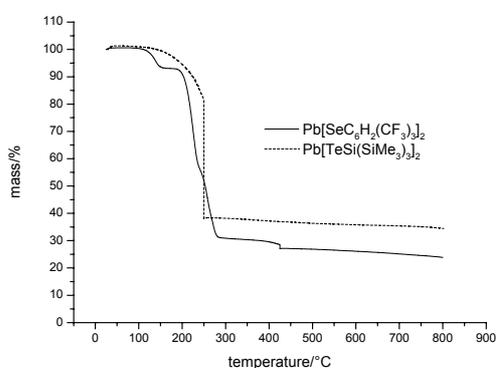


Figure 2. TG decomposition profiles of $\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ and $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$ in nitrogen atmosphere at a heating rate of 7 °C/min. The $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$ curve includes an isothermic step of 30 min at 250 °C.

The products of the thermolyses of the single-source precursors were characterized by powder X-ray diffraction (XRD). The compounds yielded the highly crystalline lead chalcogenides PbSe and PbTe, respectively (Fig. 3).

Thin films of lead selenide particles were prepared by spincoating polymer-precursor mixtures of PEO and $\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ in THF/dichloromethane with varying polymer/precursor ratios on a silicon wafer followed by thermolysis under argon at 300 °C for 15 minutes and at 425 °C for 20 minutes. The remaining silvery-grey thin films on the silicon wafer were directly characterized by scanning electron microscopy (SEM). A SEM image

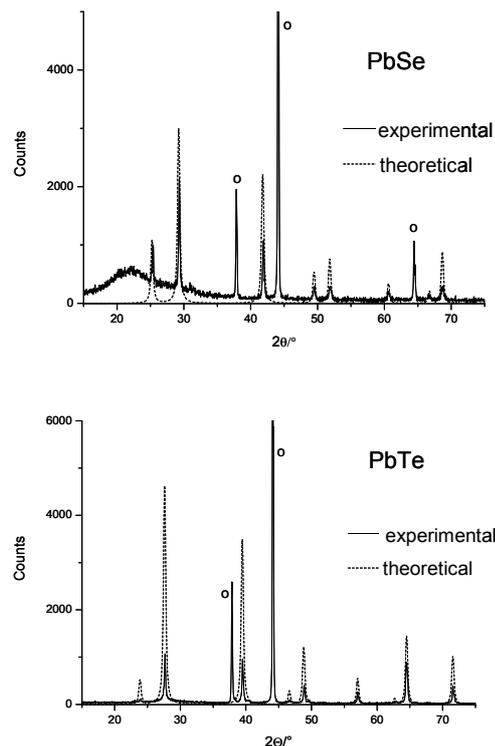


Figure 3. X-ray powder diffraction patterns of the thermolyzed products of $\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ and $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$. Reflections indexed with a ring derive from the aluminum sample holder. PDF-numbers of the theoretical patterns: 6-345 (PbSe) and 38-1435 (PbTe).

of the particle film obtained from a polymer/precursor mixture with a 1:1 ratio (Fig. 4a) shows lead selenide particles with an average diameter of 50 nm. When a polymer/precursor ratio of 1.4:1 was used, the particles were found to be more agglomerated and showed a larger size dispersion (Fig. 4b).

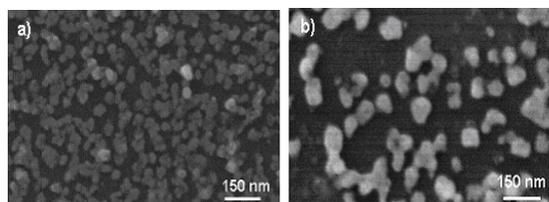


Figure 4. (a) SEM image of a film of PbSe particles obtained from a polymer/precursor mixture with a 1:1 ratio. (b) SEM image of a film of PbSe particles obtained from a polymer/precursor mixture with a 1.4:1 ratio.

In the case of even higher PEO/precursor ratios of 1.8:1 or 2:1 no individual particles

but only extended particle aggregates of irregular size were observed. This series of experiments makes clear that a minimum concentration of the precursor in the mixture is required to obtain lead selenide particles of defined size and a good homogeneity of the particle film.

The particles could be detached from the silicon wafers using ultrasound and were transferred in aqueous suspension to carbon coated copper grids for transmission electron microscopy (TEM) investigations. Identification as PbSe could be achieved by high resolution TEM (HRTEM) and electron dispersive X-ray analysis (EDX). An overview image (Fig. 5a) confirmed the particle size of 40-50 nm. In HRTEM images we identified the (200) lattice planes of PbSe (Fig. 5b) with a lattice spacing of $d = 3.04 \text{ \AA}$.

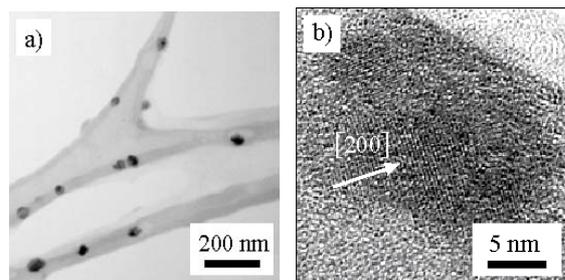


Figure 5. (a) TEM image of the PbSe particles after detachment from the Si wafer. (b) HRTEM image of the isolated PbSe particles.

The identity of the particles as pure lead selenide was also found by energy dispersive X-ray (EDX) spectroscopy. The EDX spectrum shows signals of lead and selenium with a 1:1 atomic ratio together with those of silicon, carbon and copper stemming from the TEM grid and remaining traces of the silicon wafer the particle film was originally prepared on (Fig. 6).

A similar preparative procedure was chosen for the synthesis of thin layers of lead telluride particles. From a PEO/precursor mixture in dichloromethane with a 2:1 ratio we obtained a layer of slightly agglomerated particles of about 30 nm size (Fig. 7b) when thermolysis

conditions of 15 minutes at 250°C followed by 5 minutes at 400°C were applied.

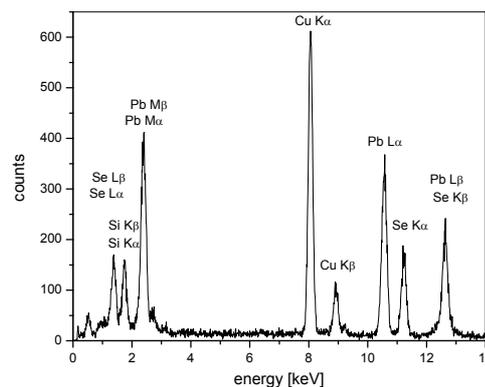


Figure 6. TEM-EDX spectrum of lead selenide particles.

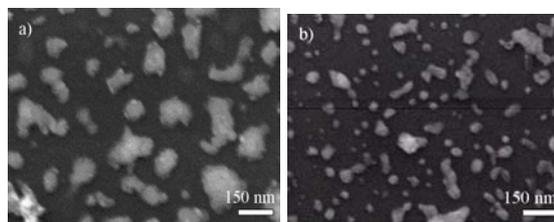


Figure 7. (a) SEM image of a film of PbTe particles obtained from a polymer/precursor mixture with a 2:1 ratio. The reaction conditions were 20 min at 250 °C and 10 min at 400 °C. (b) SEM image of a film of PbTe particles obtained from a polymer/precursor mixture with a 2:1 ratio. The reaction conditions were 15 min at 250 °C and 5 min at 400 °C.

With longer annealing times (20 minutes at 250 °C and 10 minutes at 400 °C) the particles tend to form bigger agglomerates and the layers became more inhomogeneous (Fig 7a).

Like the lead selenide particles, the lead telluride crystals could also be transferred to a TEM grid and were characterized by TEM, HRTEM and EDX. An average particle size of about 30 nm and the high degree of agglomeration found in SEM was confirmed (Fig 8a). In HRTEM images the (200) lattice planes of cubic PbTe with a d -value of 3.22 \AA were identified (Figure 8b). By EDX we found lead and tellurium in an atomic ratio of 1:1 as expected for pure lead telluride particles (Fig. 9).

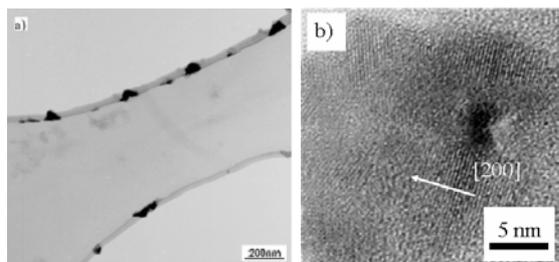


Figure 8. (a) TEM image of the PbTe particles after detachment from the Si wafer. (b) HRTEM image of the isolated PbTe particles.

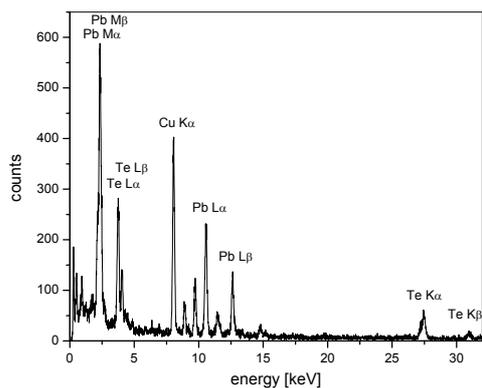


Figure 9. TEM-EDX spectrum of lead telluride particles.

Summary and Conclusions

We prepared nanoscale layers consisting of particles of the thermoelectric chalcogenides PbTe and PbSe via spincoating mixtures of a polymer and a precursor. As the thermal decomposition of the lead chalcogenide precursor takes place at lower temperatures than the degradation of the polymer, primary grains of the semiconductor are formed in the polymer matrix and grow during removal of the thermoplast. The resulting thin films of lead chalcogenide particles show particle sizes of 30 – 50 nm and can be regarded as a first step towards the production of layers of different thermoelectric chalcogenides or assemblies of alternating layers of PbSe and PbTe.

Experimental Section

The syntheses of $\text{Pb}[\text{SeC}_6\text{H}_2(\text{CF}_3)_3]_2$ and $\text{Pb}[\text{TeSi}(\text{SiMe}_3)_3]_2$ were performed according to methods described in the literature^{1,2,6,7}. In general the precursor synthesis and the preparation of polymer-

precursor-solutions were carried out in an atmosphere of dry argon. TGA was performed in corundum crucibles under a dynamic nitrogen atmosphere with a Mettler-Toledo TGA/SDTA851. XRD patterns were recorded on a Philips X'Pert-diffractometer using Cu K α radiation ($\lambda = 154.2$ pm). TEM and EDX were performed on an Philips CM 20 FEG (200 kV, LaB $_6$ -cathode). SEM experiments of the nanoparticle films on the silicon wafers were performed on a Hitachi S-4100 working with an acceleration voltage up to 30 kV. For preparing thin polymer-precursor films a spincoater from Convac was used. Generally a silicon wafer was placed on a rotatable plate with a small central opening where vacuum could be applied to fix the wafer. Two or three drops of the precursor-polymer solution were given on the silicon wafer which was then rotated with 2000 turns per minute for 60 seconds. The thickness of as-prepared polymer films was measured with the profilometer Dektak ST from Veeco Instruments. Conversion of the polymer-precursor films to nanoparticle films of PbSe and PbTe were performed under Argon atmosphere in a Schlenk glass tube placed in a tube furnace.

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