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Thermal transformation of plumbonacrite/Si films into microstructured Pb/Si ones

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ABSTRACT

In this work we report the transformation of chemically deposited plumbonacrite ($Pb_{10}O(OH)_6(CO_3)_6$) films induced by thermal annealing in nitrogen atmosphere at temperatures in the 25–700 °C range. The plumbonacrite films were deposited on silicon substrates, at room temperature, by the photo-assisted chemical bath technique using lead acetate as lead precursor and sodium citrate as the complexing agent. The thermal decomposition of plumbonacrite powder was observed by TGA. The crystalline structure and surface morphology of the as-grown and annealed films were analyzed by XRD and SEM, respectively. The results show the thermal decomposition of plumbonacrite into lead oxide at lower temperature and subsequently to elemental lead at higher annealing temperature, accompanied by drastic morphology changes. The resulting Pb films are constituted by a flat, smooth layer with emerging hemispheres of micrometric variable size, in the order of 1–5 mm. These films were partially converted to PbSe by immersion in an aqueous solution containing selenium ions.

1. Introduction

Plumbonacrite ($Pb_{10}O(OH)_6(CO_3)_6$) is a basic lead carbonate, with higher carbonate content and lower stability than hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), another basic lead carbonate [1]. Both compounds have been reported as lead corrosion products, being plumbonacrite an early corrosion product which transforms to hydrocerussite as longer term lead corrosion product [2]. Plumbonacrite has been also found as mineral in nature [3] and some few papers in literature report on the synthesis of plumbonacrite and plumbonacrite films [4–6]. In our group we have reported chemical deposition processes to obtain synthetic plumbonacrite films and shown their high reactivity, which allow easy conversion to lead oxides and lead chalcogenides by means of post-deposition treatments [6–8].

Spherical-shaped materials at the microscale level have wide applications for super-active catalyst, fast responsive sensor, optoelectronic components, and encapsulation or controlled release of sensitive materials. Different synthesis techniques are utilized to give rise to novel microspheres, like sol-gel [9], solvothermal reduction [10], laser induction [11], thermal evaporation [12] and hydrothermal method [13]. Spherical submicron-sized particles of gold from gold nanoparticles stabilized with NaCl using the laser-inducted melting technique were reported by T. Tsuji. The laser technique was also used for the synthesis of the AgGe microspheres alloy [11] with a soccer ball-like morphology. Metallic (Au, Cu, Fe, Ni) and metallic oxides (Fe_2O, NiO, TiO_2, WO_3) can be formed using an innovative selective pulsed heating method irradiating on colloidal nanoparticles [14]. Metallic zinc layered polyhedral microparticles were synthesized by thermal evaporation [12]. The hydrothermal route is another common methodology for the synthesis of metal and metal alloys microspheres. Porous Cu microspheres were synthesized using copper acetate; the materials showed a good catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol. A template-free approach to prepare three-dimensional cobalt microspheres composed of nanosheets with potential applications to catalysis, sensor and energy storage was reported in Ref. [15].

In this work, we have deposited plumbonacrite films on silicon substrates and analyzed the evolution of their crystalline structure and surface morphology induced by thermal annealing in nitrogen atmosphere. The aim of this study is to determine the crystalline lead phases and their characteristics, which are induced by the thermal annealing in chemically deposited plumbonacrite layers.

2. Experimental

The plumbonacrite films were deposited on silicon wafer halves (10 cm diameter), that were previously cleaned in HF at 10%. For

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the deposition, the wafer halves were horizontally placed at the bottom of a 100 ml beaker, where the reaction solution was formed by the sequential addition of 0.2 M lead acetate ($((CH_3COO)_2$-$Pb{\cdot}3H_2O$, 100% Baker), 0.4 M sodium citrate ($HOC(COONa)(CH_2$-$COONa)_2{\cdot}2H_2O$, 100% Baker), 0.5 M potassium hydroxide (KOH, 85% Sigma Aldrich) and deionized water. Then, the beaker was placed in a box under irradiation from a UV lamp (364 nm, 22 W) for 5 h, after which the pieces of silicon wafers with the formed layers are removed from the solution and dried with nitrogen. The thermal treatments of the plumbonacrite films were carried out for 1 h in a tubular furnace with a quartz tube and controlled atmosphere. The samples were placed in the center of the furnace and a N_2 atmosphere was introduced at 1 L/min rate. Then, the temperature rises at 300 °C, 500 °C and 700 °C at a rate of 20 °C/min. The plumbonacrite film treated at 700 °C was introduced in 10 mL of Se^- aqueous solution for 45 min to promote the conversion to PbSe. The crystalline structure of the samples was analyzed by X-ray diffraction technique using a Rigaku DMax

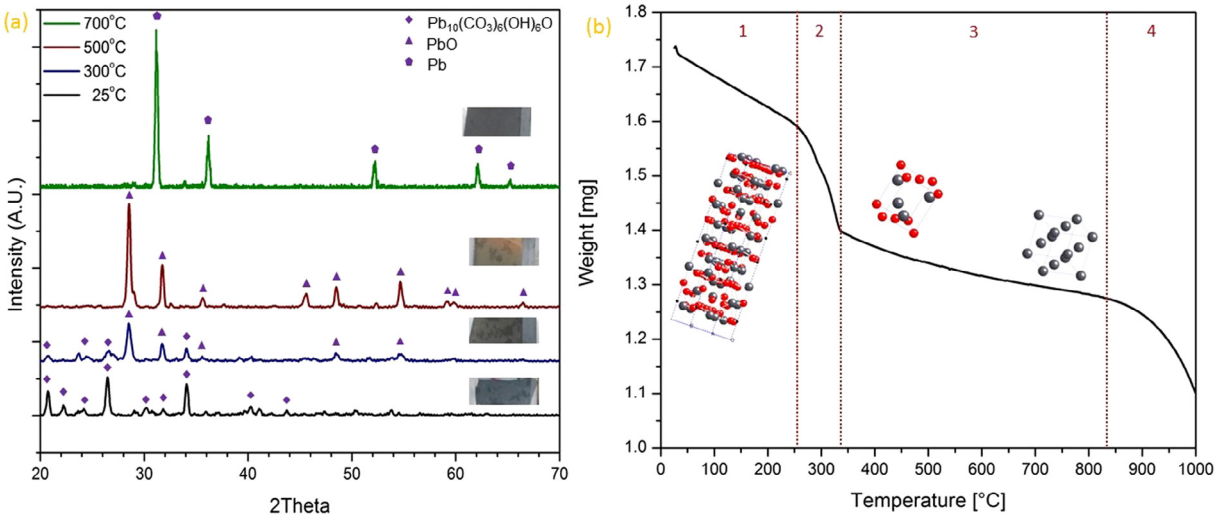

Fig. 1. X-ray diffraction patterns of the plumbonacrite films, from bottom to top, at room temperature, 300 °C, 500 °C and 700 °C.

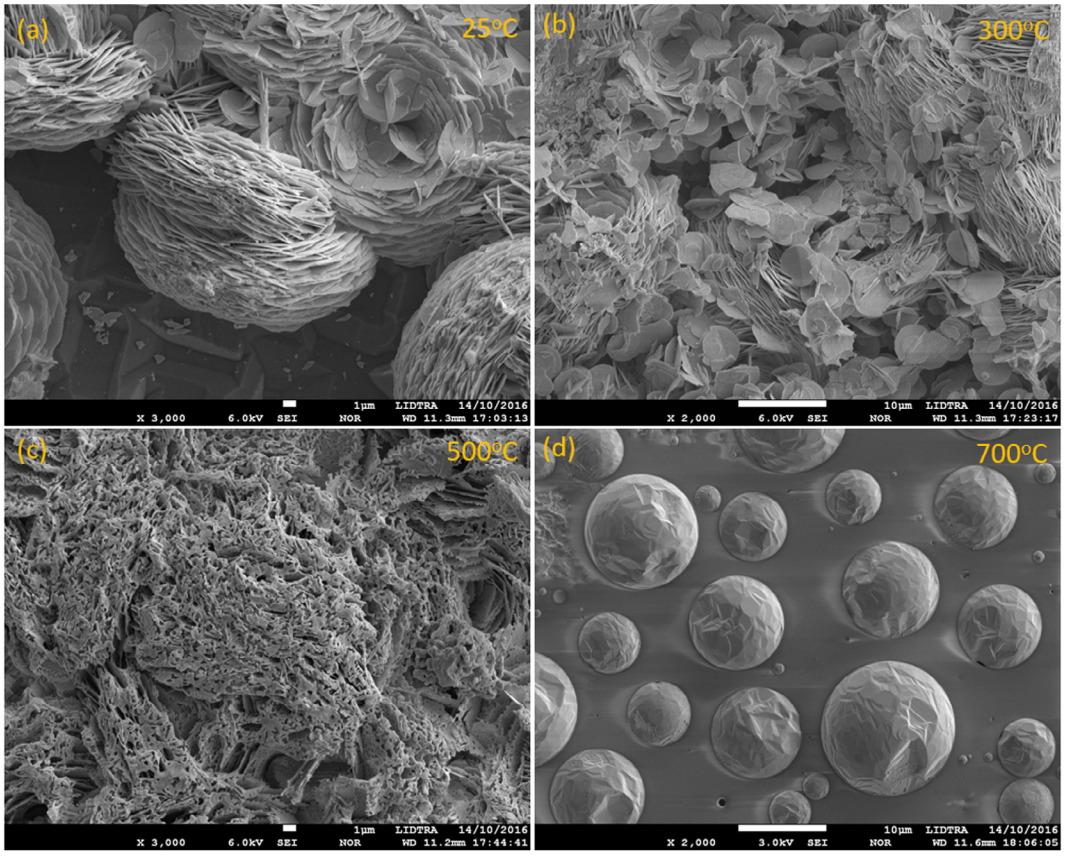

Fig. 2. SEM images of the plumbonacrite films at room temperature (a), treated at 300 °C (b), 500 °C (c) and 700 °C (d) for 1 h under N_2 atmosphere.