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Thermochimica Acta 382 (2002) 297–301

thermochimica acta

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Synthesis of nanocrystalline silicon in the system La–Si–H–Cl: thermoanalytical investigations

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Received 29 May 2001; accepted 14 June 2001

Abstract

The heterogeneous reaction of lanthanum or lanthanum(III) chloride with a gas mixture of hydrogen and silicon tetrachloride is a novel synthesis route for silicon nanocrystals. The reaction product consists of $LaCl_3$ and about 10 wt.-% Si. The silicon does not give X-ray powder diffraction signals. After the separation brown nanocrystalline silicon remained, with an average size of 5 nm. Conclusions about the state of the silicon in the $LaCl_3$ matrix are drawn by the thermal characterization of the reaction product. The thermal analysis curve of the reaction product shows, at the first cycle, an endothermic effect, which is about 8 K higher than the melting point of $LaCl_3$. This marks a strong interaction between silicon and $LaCl_3$, which is irreversibly lost after thermal treatment.

Keywords: Nanocrystalline silicon; Thermal analysis

1. Introduction

The application of nanocrystalline, porous or amorphous silicon in optoelectronic devices forces the search for practicable preparation routes [1–3]. A novel preparation route to deposit nanocrystalline silicon is the heterogeneous reaction of lanthanum or lanthanum(III) chloride with a gas mixture of hydrogen and silicon tetrachloride at temperatures above 750 °C. After the reaction, a brown, voluminous and air sensitive product is removed from the reactor. The chemical analysis shows a molar ratio of La:Si:Cl of 1:1:3, corresponding to the composition $LaCl_3{\cdot}Si$. The X-ray powder diffraction pattern of the product shows only reflexes of anhydrous $LaCl_3$ and no indication of silicon. Reflexes of silicon are only found after annealing the product in sealed and evacuated quartz ampoules (10^{-8} bar) at 800 °C. The silicon nanoclusters are separated from the $LaCl_3$ by dissolving the product in acetic acid. Analysis by transmission electron microscopy (TEM) and Raman spectroscopy show an average size of the particles in the range of 3–5 nm. In aqueous solution they gradually form 10 to 50 nm large agglomerates. The X-ray powder diffraction patterns of the untreated reaction product (a); the annealed sample (b) and the separated, agglomerated silicon (c) are shown in Fig. 1. The details of the synthesis and the characterization are reported in [4].

The mechanism of silicon nanocluster deposition is not yet known. However the metal involved clearly plays the key role, because silicon deposition requires the formation of the metal chloride. By reaction of a

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0040-6031/02/$ – see front matter
PII: S0040-6031(01)00755-9

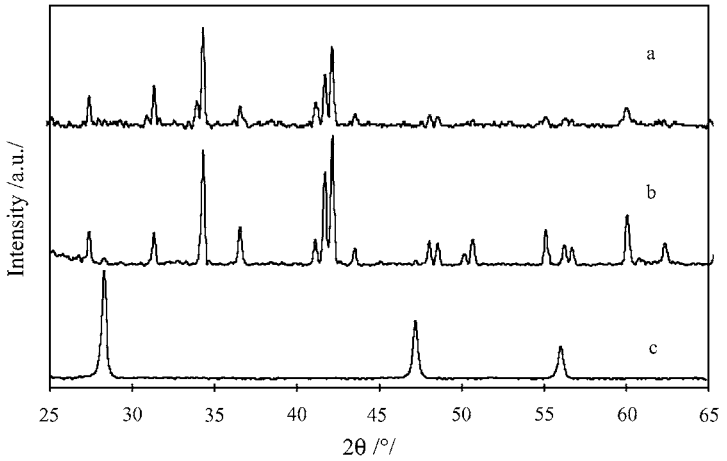

Fig. 1. X-ray pattern of the reaction product with $LaCl_3$ (a); the annealed sample (b) and the agglomerated silicon (c).

gas mixture of silicon tetrachloride and hydrogen with a metal, either a metal chloride or a silicide is formed. Gaseous reaction products are hydrogen chloride and chlorosilanes, in some cases monosilane [5,6]. Whether the metal chloride or the metal silicide is formed can be derived from an analysis of Gibbs energy of the formation of the chlorides (Fig. 2), [7]. As a general rule, metal chlorides are formed if their free enthalpy of formation is lower than −320 kJ/mol. Above that value, a formation of metal silicide is to be expected (according to the stoichiometry in Eq. (1).

$$\frac{4}{x}\mathrm{MCl}_x + \frac{x+4y}{x}\mathrm{Si} \leftrightarrow \frac{4}{x}\mathrm{MSiy} + \mathrm{SiCl_4(g)} \qquad (1)$$

Another requirement for silicon deposition is a low partial pressure of the metal chloride, e.g. silicon nanoclusters are not deposited in a manganese chloride

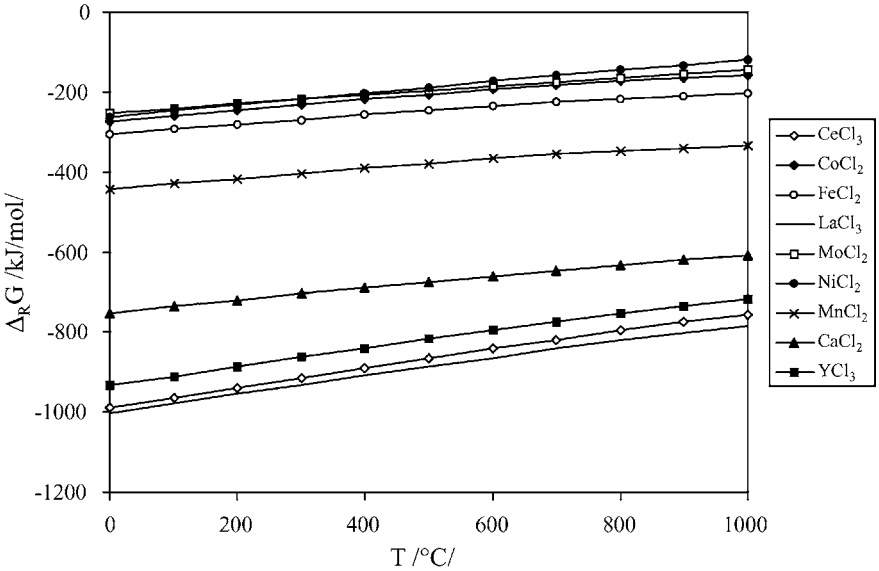

Fig. 2. Gibbs energy of formation of the chlorides depending on the temperature.

matrix. Apart from La, the metals Y, Ce and Ca are promising candidates for silicon deposition from the gas phase (Fig. 2).

$LaCl_3$ is supposedly not present as a pure phase under reaction conditions. From thermodynamic aspects, instead a solubility of silicon tetrachloride and/or a solubility of reactive precursors of the silicon nanocluster in $LaCl_3$, respectively the formation of a yet unknown La–Si–Cl–(H) compound could be given. In any case, the obtained reaction product should exhibits a history, which can be followed by thermal analysis. Hence, the thermal characterization of the reaction product is a contribution to the understanding of the state of the silicon in the $LaCl_3$ matrix.

2. Experimental

Used raw materials are anhydrous lanthanum chloride (Alfa, 99.99 %), lanthanum (Alfa, 99.99 %), and for comparative measurements, anhydrous lanthanum chloride (Aldrich, 99.99+%), and silicon powder (Alfa, 99.9985%). Differential thermoanalytical measurements were conducted under argon atmosphere (Air liquid, 99.999%) in alumina crucibles in a Setaram Q-DTA1600. A Siemens D5000 was used for X-ray powder diffraction measurements. Due to the high sensitivity of lanthanum chloride against moisture, all preparations were carried out in a glove box (Braun, $O_2 < 4$ ppm, $H_2O < 5$ ppm).

3. Results and discussion

The $LaCl_3$/Si reaction product was cycled in the differential thermal analysis (DTA) apparatus between 800 and 900 °C around the melting point of pure $LaCl_3$ (852 °C). Fig. 3 shows the DTA curves of seven successive cycles. The DTA curve of the first cycle displays one endothermic effect that is 8 K higher than the melting point of pure $LaCl_3$. The effect is lost in subsequent scans, where only the endothermic signal of the melting of $LaCl_3$ remains. The powder diffraction pattern of the cycled sample shows characteristic lines of silicon. After annealing of the reaction product at 900 °C over three weeks in evacuated quartz ampoules, a separation of the silicon from the $LaCl_3$ matrix occurred [4]. Separation into crystalline silicon and $LaCl_3$ is yielded by both methods, but the DTA cycling shows up as a distinctively more rapid process.

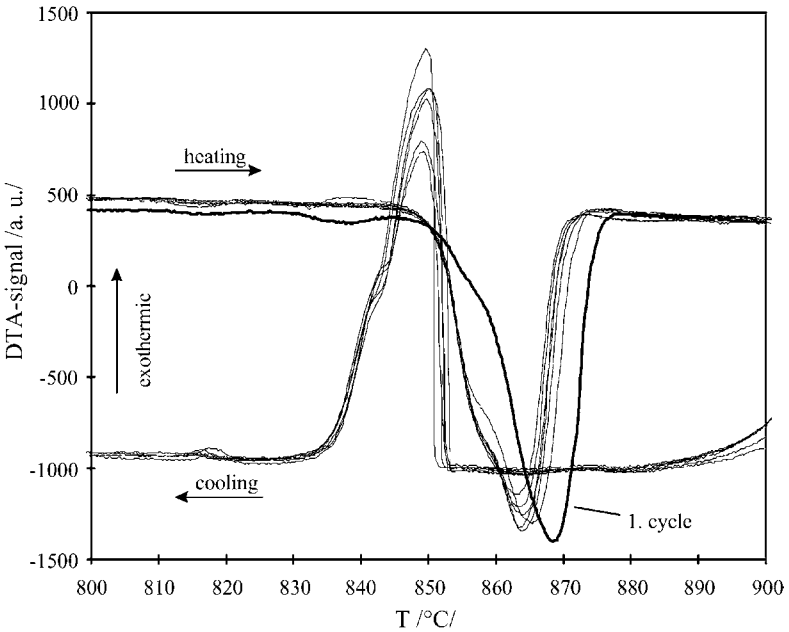

Fig. 3. Differential thermal analysis of the reaction product $LaCl_3$/Si.

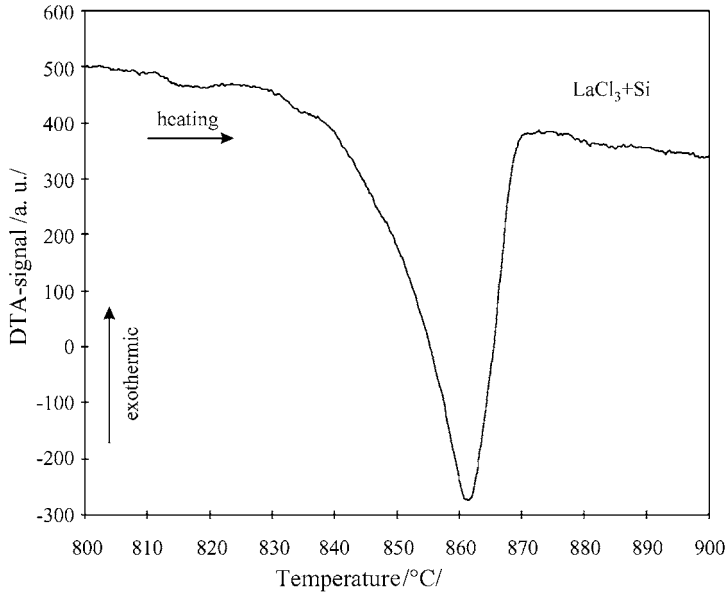

Fig. 4. DTA curve of a mixture of $LaCl_3$ and Si.

To answer the question, whether the first cycle signal arises from the reaction product or if this signal has to be attributed to a chemical reaction between silicon and $LaCl_3$, the following experiments were carried out. A mixture of silicon and anhydrous lanthanum chloride was annealed for four weeks at 700 °C in a sealed and evacuated ampoule. In spite of long time of annealing, no reaction occurred. The annealed mixture yielded a DTA curve pattern (Fig. 4) comparable to the second or higher cycle of the reaction product (Fig. 3) and shows only the melting signal of $LaCl_3$.

The endothermic DTA signal of the first run at 860 °C indicates a strong interaction between silicon and lanthanum chloride, which is lost irreversibly in the following cycles. Thus, the reaction product cannot be understood as a simple mixture of lanthanum chloride and silicon. It can be assumed that during the reaction of La or $LaCl_3$ with the $SiCl_4/H_2$ mixture a ternary or quaternary compound consisting of La, Si, Cl, and perhaps H is formed in a solid-gas reaction. During the first DTA run, remaining traces of this unknown compound are decomposed and their gaseous decomposition products are flushed away with the argon stream. As a support to our assumption, ternary rare earth silicide halogenides are known [8–10]. In the La–Si–Cl system, the compound $La_3Cl_2Si_3$ has been found [10]. The existence of silicon in a solid metal chloride matrix might be possible due to a coordination of silicon by chlorine atoms of the chloride. In an extreme formulation, a similar state as it exists in metal hexafluorosilicates or in the suggested hexachlorosilicate [11] might be reasonable to consider.

4. Conclusions

By means of thermal analysis, a strong interaction between silicon and the lanthanum chloride matrix could be established in the $LaCl_3$/Si reaction product that is lost after thermal treatment of the reaction product. The existence of the ternary compound $La_3Cl_2Si_3$ [10] could be an indication to analogous compounds, which are stable under the reaction temperature and $H_2/SiCl_4$-gas atmosphere. Lowering of the temperature leads to the decomposition of this compound under deposition of nanocrystalline silicon in a $LaCl_3$-matrix.

According to a thermodynamic consideration based on the free Gibbs energy of formation of the chlorides, all metals forming stable chlorides under these reac-

tion conditions should be able to deposit silicon from the gas phase. In this way, a silicon deposition in YCl_3 was already demonstrated [4].

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