



## Methylated silicon: A longer cycle-life material for Li-ion batteries



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### H I G H L I G H T S

- Thin layers of amorphous methylated Si were prepared by PECVD.
- We studied this material as a negative electrode material for Li-ion batteries.
- Amorphous methylated Si shows enhanced cyclability compared to pure Si.
- The improvement is attributed to mechanical softening of amorphous Si.

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### A B S T R A C T

Using Plasma Enhanced Chemical Vapor Deposition, one can prepare methylated amorphous silicon thin-layer anodes for Li-ion batteries exhibiting good cyclability. The properties of that material are investigated here in view of this target application. In comparison with pure amorphous silicon prepared in the same conditions, the improvement is twofold: longer lifetime, and capability of working with thicker electrodes. For example, capacity retention after 100 cycles of 150 nm thick layers with 10% carbon content is almost 70% larger than that of pure a-Si layers. The observed improvement is attributed to mechanical softening of amorphous Si by incorporation of CH<sub>3</sub> groups.

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## 1. Introduction

Silicon is considered as a promising anode material for Li-ion batteries because of its unique capability to insert large quantities of lithium: its capacity (about 4000 mA h g<sup>-1</sup>) is more than ten times as high as that of graphite, which is used in commercial batteries. However, its use is severely limited, due to the important swelling of the material in the loaded state (300%) [1]. Various solutions to this problem were proposed: they require the use of silicon in nanometric form: several reviews summarize the recent literature on this subject [2–4].

Although they are not of practical interest for applications requiring large amounts of energy, thin layers of amorphous silicon are currently studied (see for example Ref. [2]), in particular

because they offer a very convenient geometry for many experimental studies. Magnetron sputtering, evaporation, Chemical Vapor Deposition (CVD) were used to produce these layers.

Various treatments of the layers were shown to improve their cyclability [2,5–7]. However, in most cases, the cyclability is strongly reduced upon increasing the layer thickness [8]. Obviously, an improvement of the starting material properties is of great interest. Our aim here is to propose such a new starting material, with a capacity similar to that of silicon and enhanced cyclability.

Amorphous hydrogenated silicon (a-Si:H) is a particular variety of amorphous silicon: it was extensively studied because of its good semiconducting properties, due to its high hydrogen content. Part of these hydrogen atoms are linked to Si atoms, saturating most of the dangling bonds which are present in the non-hydrogenated amorphous material. This lowers the density of electronic states in the forbidden band gap, hence good semiconducting properties are obtained [9]. This semiconductor may be doped either n- or p-type.

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a-Si:H was also considered as an anode material for Li-ion batteries: for instance, Kulova et al. [10] studied lithium insertion into amorphous hydrogenated silicon prepared by rf glow discharge in silane. They confirmed the cyclability decrease of the layers with increasing their thickness.

The use of heterogeneous mixtures of carbon and silicon (powders of silicon grains surrounded by carbon, etc...) allows for improving the cycling properties of silicon [11]. Such heterogeneous mixtures have focused attention because the stoichiometric alloy SiC (silicon carbide) does not insert lithium. Indeed SiC is known for its electrochemical inactivity and is currently used as an inactive phase in a variety of anode composites (see for example Ref. [12]). However, even in such mixtures, volume changes due to insertion/de-insertion of lithium remain an important issue.

In this paper we disregard these composite materials and consider a particular form of Si–C alloy as an anode material for Li-ion batteries. This alloy is a homogeneous amorphous silicon/carbon based material where the C atoms are inserted into amorphous silicon as methyl groups CH<sub>3</sub>. This silicon-rich material can be expected to retain a high lithium-insertion capability. Like silicon–silicon carbide composites it may be expected to exhibit a behavior distinct from that of pure silicon, while avoiding disadvantages associated with heterogeneous mixtures. The purpose of the present work was therefore to investigate the performance of methylated amorphous silicon as a negative electrode material for lithium-ion batteries.

## 2. Methylated silicon

Thin films of amorphous Si–C alloys can be prepared by simultaneous decomposition of silane and methane obtained by Plasma Enhanced Chemical Vapor Deposition (PECVD). Using this technique, one can obtain a variety of amorphous silicon–carbon alloys [13].

In the present paper, thin films of the amorphous material are obtained in the “low power regime” (plasma power  $P < 0.3 \text{ W cm}^{-2}$ ) [13,14], where only SiH<sub>4</sub> molecules are decomposed (not CH<sub>4</sub> molecules): carbon incorporation into the amorphous Si layer is then produced by the reaction between methane molecules and active species (radicals) resulting from the decomposition of SiH<sub>4</sub>. In this low-power regime the carbon content can only be obtained in a restricted range  $x < 0.4$ . Carbon atoms are then only or mostly inserted as methyl groups –CH<sub>3</sub> [13,15]. The material may thus be described as methylated amorphous silicon, with composition a-Si<sub>1-x</sub>(CH<sub>3</sub>)<sub>x</sub>:H.

These methyl groups can only be linked to one silicon atom, thus creating dead ends in the silicon network. They were shown to be surrounded by spherical nanovoids [16]. The presence of a majority of silicon atoms should confer a high lithium intercalation capacity to the material. The fact that the carbon content may be continuously tuned between 0 and 0.4 is another advantage, enabling to choose the optimum content for the target application.

For compounds with a proportion of carbon higher than 0.2, not all of the carbon atoms are in CH<sub>3</sub> configuration: part of the carbon atoms is in CH<sub>2</sub> configuration. This is also the case for the material deposited with a high-power plasma ( $P > 0.3 \text{ W cm}^{-2}$ ): the value of the carbon proportion  $x$  may then be obtained in the whole range  $0 < x < 1$  [13,14].

The relative proportion of CH<sub>2</sub> and CH<sub>3</sub> configurations was estimated in Ref. [13] from comparison between hydrogen and carbon contents in the material. In the present study, they are directly monitored by infrared spectroscopy measurements (see Section 4).

## 3. Experimental conditions

Different layers of pure a-Si:H and a-Si<sub>1-x</sub>(CH<sub>3</sub>)<sub>x</sub>:H were prepared by PECVD in the low-power regime.

For electrochemical measurements, layers with different thicknesses were deposited on stainless steel substrates. Before deposition the substrates were first washed with a concentrated detergent, then rinsed with milli-Q water, and dried with a nitrogen flow. Then they were placed in the PECVD chamber, where they were submitted to a hydrogen plasma (pressure 200 mTorr, power density  $100 \text{ mW cm}^{-2}$ ) for 5–10 min. This pre-treatment enabled good adhesion of the layer. Carbon content in the film was controlled through the gas-phase composition, i.e., [CH<sub>4</sub>] partial pressure in the [CH<sub>4</sub>][SiH<sub>4</sub>] mixture [13]: the investigated carbon contents were  $x = 0$ ,  $x = 0.1$ ,  $x = 0.15$ ,  $x = 0.2$ ,  $x = 0.25$  and  $x = 0.33$ . Thicknesses ranged from 30 to 150 nm for  $x = 0$  and from 50 to 600 nm for  $x = 0.1$  to 0.2. For  $x = 0.25$  and  $x = 0.33$ , only a restricted series of samples was studied (see below), with thicknesses 45 nm and 30 nm respectively. During film deposition, the substrate temperature was maintained at 250 °C. No intentional doping was performed (i.e., no gas such as B<sub>2</sub>H<sub>6</sub> or PH<sub>3</sub> was added to the SiH<sub>4</sub>/CH<sub>4</sub> mixture).

Two-electrode half-cells were assembled in order to evaluate the electrochemical properties. The a-Si<sub>1-x</sub>(CH<sub>3</sub>)<sub>x</sub>:H thin films were used as the working electrode. Li-metal sheet (99.9% purity, Aldrich) was used as the counter electrode. The electrolyte was 1 M LiClO<sub>4</sub> (battery grade, 99.99% purity, Aldrich) in propylene carbonate (99.7% purity, Sigma–Aldrich). The cells were cycled galvanostatically. Lithiation of the a-Si<sub>1-x</sub>(CH<sub>3</sub>)<sub>x</sub>:H electrode was carried out from the initial open-circuit voltage down to 0.025 V, then cycling was performed between 0.025 V and 2 V vs. Li/Li<sup>+</sup>. Cells were tested at various charge/discharge current densities in the C/0.5–C/10 range (full charge or discharge in 0.5–10 h, corresponding to current densities from 2 to 50  $\mu\text{A cm}^{-2}$ , depending on carbon content and film thickness). A multi-channel potentiostat (VMP2, Bio-Logic) was used to perform the electrochemical measurements. All of the experiments were performed at room temperature (23 °C).

The film thickness was controlled by the deposition time, after proper calibration of the PECVD reactor [14], using optical measurements for determining refractive index and thickness of the deposited layer. Knowing the film thickness, the density of the material must be known to determine the mass of active material. A precise measurement of this density is not an easy task. Very few data are available in the literature. Solomon et al. [13] reported that the  $x = 0.1$  compound density was  $2 \text{ g cm}^{-3}$ , compared to  $2.25 \text{ g cm}^{-3}$  for pure a-SiH. Williamson et al. studied materials very similar to ours [16]. They reported densities decreasing almost linearly from 2.26 for pure a-Si:H to 1.38 for a carbon content  $x = 0.3$ . Assuming this linear relationship, we estimated the following values for the different carbon contents used in this study: for  $x = 0.1$ ,  $d = 1.93$ ; for  $x = 0.15$ ,  $d = 1.79$ ; for  $x = 0.20$ ,  $d = 1.65$ ; for  $x = 0.25$ ,  $d = 1.51$  and for  $x = 0.33$ ,  $d = 1.29$ .

After cycling, the cells were opened in the glove box, and the layers were rinsed successively in propylene carbonate and in a mixture of ethylene carbonate and dimethyl carbonate. They were dried under vacuum before post-mortem observation.

For infrared absorption measurements, Si<sub>1-x</sub>(CH<sub>3</sub>)<sub>x</sub>:H layers were deposited on a crystalline silicon substrate (double-side polished parallel plate, 500  $\mu\text{m}$  thickness, cut from a low-doped float-zone silicon wafer). The infrared transmission of the layers was measured using a non-polarized IR beam and at 45° incidence angle. This geometry allows to avoid the oscillations due to multiple reflections within the parallel-plate substrate, often observed when normal incidence is used. Layers with 0.1, 0.2, 0.3 and 0.37

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