Mesoporous Si and multi-layered Si/C films by Pulsed Laser Deposition as Li-ion microbattery anodes

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Abstract. Silicon is a very attractive Li-ion battery anode material due to its high theoretical capacity, but proper nanostructuring is needed to accommodate the large volume expansion/shrinkage upon reversible cycling. Hereby, novel mesoporous Si nanostructures are grown at room temperature by simple and rapid Pulsed Laser Deposition (PLD) directly on top of the Cu current collector surface. The samples are characterised from the structural/morphological viewpoint and their promising electrochemical behaviour demonstrated in lab-scale lithium cells. Depending on the porosity, easily tuneable by PLD, specific capacities
approaching 250 µAh cm$^{-2}$ are obtained. Successively, newly elaborated bi-component silicon/carbon nanostructures are fabricated in one step by alternating PLD deposition of Si and C, thus resulting in novel multi-layered composite mesoporous films exhibiting profoundly improved performance. Alternated deposition of Si/C layers by PLD is proven to be a straightforward method to produce multi-layered anodes in one processing step. The addition of carbon and mild annealing at 400 °C stabilize the electrochemical performance of the Si-based nanostructures in lab-scale lithium cells, allowing to reach very stable prolonged reversible cycling at improved specific capacity values. This opens the way to further reducing processing steps and processing time, which are key aspects when upscaling is sought.

**Keywords:** silicon, mesoporous, pulsed laser deposition, anode, lithium battery

**Introduction**

In the last decade, we are dealing with the rapid development of high performing portable electronic devices, such as smart phones and notebooks, which are becoming more and more demanding in terms of energy requirements. This continuously leads to a strong demand for new sources of power able to provide high capacity and high energy densities. In such a scenario, the Li-ion battery (LIB) is recognized as the system of choice. Today’s LIBs partially satisfy the present demands, but there is still room for further improvements$^1$. 

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$^1$
As far as the anode material is concerned, commercial graphite shows excellent capacity retention during battery cycling. Nevertheless, despite its good cycling stability and low cost, the low theoretical capacity of 372 mAh g\(^{-1}\) is clearly insufficient for the huge demands of the next generation of high energy density electronic devices as well as electric vehicles\(^2\). To meet these requirements, several elements that can reversibly alloy with lithium were investigated, including Si, Sn, Al, Ge, as well as mixed compounds thereof\(^3\)\(^–\)\(^6\). Because of its exceptional theoretical capacity exceeding 4000 mAh g\(^{-1}\), silicon is one of the most promising candidates among these elements to be used as anode material, as demonstrated by the intensive investigations recently carried out on this subject. The main limitations to its wide spread application are the extremely high volume change (~300 %)\(^7\) occurring during reversible reaction with lithium and leading to mechanical fragmentation and active material particle pulverization. Nanostructuring, introduction of voids and addition of other active materials having lower capacity (e.g., carbon) are the main routes currently under exploitation to bypass this drawback. The advantages of nanostructuring have been evidenced in recent works, which demonstrated the existence of a threshold dimension in silicon particles that prevents from crack propagation upon lithiation\(^8\)\(^–\)\(^10\). The introduction of pores in the silicon anodes is another well-known strategy to face the detrimental effects of volume variation\(^11\)\(^–\)\(^13\); indeed, depending on their size and distribution, voids can accommodate the expansion during lithiation, mitigate internal stresses and possibly prevent from fragmentation and detachment from the current collector. Porous Si films are generally prepared via electrochemical etching using hydrofluoric acid \(^14,15\) or by electrodeposition \(^16\)\(^–\)\(^18\).
In this work, we explore the possibility of growing mesoporous hierarchical amorphous silicon nanostructures by simple and rapid Pulsed Laser Deposition (PLD). As it allows to easily tailor the film morphology at the nanoscale, both in terms of nanostructuration and introduction of voids, PLD enables a straightforward engineering of the anode material properties. In our silicon anodes, we introduced a controlled porosity to buffer the volume expansion; moreover, the preferential growth in the direction perpendicular to the substrate headed to favouring the electronic and ionic transport through the electrode. Different films were fabricated having different morphology and degree of porosity. The effect of an increasing porosity was studied at ambient temperature by electrochemical testing in lithium cell configuration with liquid electrolyte. The best performing sample allowed for good initial capacity over the initial 30 galvanostatic discharge/charge cycles. Successively, in order to improve the electrochemical behaviour, both in terms of overall specific capacity output as well as capacity retention and stability upon prolonged cycling, novel multi-layered Si-C nanostructured composite films were produced. Graphite-like C has the role to improve the overall electrical conductivity (intermediate layers) and to promote the formation of a stable SEI (top layer). Moreover, mild annealing at 400 °C was adopted on these structures, in order to improve the mechanical properties in terms of stress relaxation and adhesion to the Cu current collector, thus to effective increase the stability upon cycling.

A previous work by some of the authors demonstrated good electrochemical performances of an anode made by a mesoporous Si film grown by PLD covered by a C layer grown by Chemical Vapour Deposition at 800°C\textsuperscript{19}. Here we deeper investigate the properties of mesoporous Si grown by PLD, on the way to optimize the film for microbattery anodes. Based on this optimization, we propose a simplified process to
obtain novel multilayered Si/C film where Si and C are both deposited by PLD, followed by a mild annealing at 400°C. Reducing processing steps and processing time is one of the key aspects when upscaling is sought.

**Methods**

**Preparation of mesoporous Si films**

Mesoporous Silicon films were grown by PLD under ambient conditions. A rotating and translating Si crystalline wafer (monocrystalline CZ, n⁺-doped <100>) was ablated by a KrF pulsed laser (248 nm, ~5 J cm⁻², 20 Hz, target-to-substrate distance 50 mm) under controlled atmosphere (mixture of < 3 % vol. H₂ in Ar as background gas) in a vacuum chamber, previously evacuated at 3×10⁻³ Pa. In order to grow films having different morphology and porosity, samples were produced under varying background pressures of 40, 60 and 100 Pa, respectively. Correspondingly, samples are named Si-40, Si-60 and Si-100, where the number is the deposition pressure for Si. Deposition times were set to obtain film thickness of 1µm. By increasing the background gas pressure, higher porosity can be introduced in the film by means of inducing the formation of bigger clusters during flight with a lower kinetic energy and, hence, a less-packed film on the substrate. Details on the relationship between process parameters and morphology of the Si films are reported in a previous work.²⁰ After native oxide removal by means of citric acid, copper discs were used as a substrate for Si deposition, so to act as the current collector for the active anode material in lithium cell.
Fabrication of multi-layered composite Si-C films

Composites films with desired morphology were grown by PLD adjusting the background gas pressure (Ar:H\textsubscript{2}) for each deposition, so that cluster nucleation and growth could be to some extent controlled and, hence, the film porosity. Si was deposited under 40Pa Ar:H\textsubscript{2}, while C was deposited at 5Pa Ar:H\textsubscript{2} (namely, sample Si/C-40). Deposition time for C was fixed to obtain a 70 nm-thick layer, i.e. one third of the \(~\sim\)200 nm-thickness of each coupled Si-C layer, while for Si layers grown at different pressures the deposition time was tuned to have a \(~\sim\)130 nm-thick layer, thus obtaining a final overall film thickness of 1 \(\mu\)m. This \(\mu\)m thickness was chosen to allow for comparison with the other approaches described in this article, while the parameters for deposition of C (i.e., gas pressure and time) were set so as to obtain a uniform layer able to cover the underlying Si. The C-layer relative thickness was a non-optimized starting point balancing on the one hand the need for a well-defined C layer, possibly able to pin Si expansion, and on the other hand to have enough Si to consider the final anode as Si-based. We chose to deposit Si and C by means of two separate targets mounted on a switchable target holder to grow alternatively Si or C into a multi-layered composite film. After deposition of the desired amount of one material, the laser was stopped for a while and the target holder switched without opening the vacuum chamber, thus exposing the other target to ablation. The resulting multi-layered sample was then annealed in a closed furnace filled with Ar:H\textsubscript{2} to relieve internal mechanical stresses and possibly promote adhesion of the Si layer to the copper substrate, as proven by experimental results described in ref. \cite{19}. The heating rate was set at 4 °C min\textsuperscript{−1} up to the temperature of 400 °C, hold for 5 minutes at 400 °C and then let cool down.
Characterization of the materials

In order to characterize their morphology and thickness, cross-sectional views of the single- as well as multi-layered Si films were acquired by a Supra 40 Zeiss Field Emission Scanning Electron Microscope (FESEM, accelerating voltage 3-5 kV).

Specific surface area (SSA) was determined on a Quadsorb evo™ (Quantachrome Instruments) using the Brunauer, Emmet, Teller (BET) method. Prior to adsorption, approximately 100.0 mg of solid were placed in the cell and evacuated at about 50 °C for 2 h and, successively, at 200 °C for 3h.

Raman spectra were acquired on the Si and Si/C samples upon excitation by the second harmonic (532 nm) of an air-cooled Nd:YAG laser. Laser power was kept below 0.4 mW (sample surface) while sampling Si films, in order to avoid laser-induced annealing effects. Spectra were recorded in the range 100-1800 cm\(^{-1}\) in the Stokes region and were calibrated against the 520.5 cm\(^{-1}\) line of an internal silicon wafer reference. The signal-to-noise ratio was enhanced by repeated acquisitions.

Van der Pauw measurements were performed on the samples Si/C-40 either annealed or not, in order to estimate the film conductivity in the two cases. The measurement was carried out at ambient conditions by a Hall Effect measurement Instrument (Microworld-HMS5300, heated stage AMP55), equipped with a permanent magnet (0.5T) and golden fingers with applied current below 20nA.

The electrochemical response in liquid electrolyte of the samples was tested in polypropylene three-electrode T-cells assembled as follows: a Si film disk (area 0.785 cm\(^2\)) as the working electrode, a 1.0 M lithium hexafluorophosphate (LiPF\(_6\), Solvionic, France, battery grade) in a 1:1 w/w mixture of ethylene carbonate (EC) and dimethyl
carbonate (DMC) electrolyte solution soaked on a Whatman® GF/A separator and a lithium metal foil (high purity lithium foils, Chemetall Foote Corporation) as the counter electrode. For cyclic voltammetry (CV), a second lithium foil was added at the third hole of the cell, in direct contact with the electrolyte, acting as the reference electrode. Galvanostatic discharge/charge cycling (cut off potentials: 0.02 – 1.5 V vs. Li⁺/Li) and CVs (between 0.02 and 1.5 V vs. Li⁺/Li, at 0.1 mV s⁻¹) were carried out at ambient temperature on an Arbin Instrument Testing System model BT-2000. Clean electrodes and fresh samples were used for each test. Procedures of cell assembly were performed in the inert atmosphere of a dry glove box (MBraun Labstar, O₂ and H₂O content < 1 ppm) filled with extra pure Ar 6.0.

**Results and discussion**

**Characterization of mesoporous Si films**

In the present work, a very simple single-step PLD process allowed to obtain vertically oriented thin films of mesoporous nanostructured silicon, as evidenced by FESEM analysis for morphological characterisation. The length of the columnar nanostructures was found to be approximately 1 µm, as shown in images (a), (c) and (e) of Figure 1, where the low magnification cross-sectional views of the different amorphous silicon films are depicted.
Figure 1 Cross-sectional FESEM images showing the different morphology of the mesoporous single-layered Si nanostructured films grown at increasing background gas pressure: (a, b) 40Pa, (c, d) 60Pa, (e, f) 100Pa.

The fabrication method was chosen and tuned to grow hierarchical films featured by aggregation of clusters in a columnar mesoporous algae-like structure (see images b, d, f in Figure 1). This was meant, on the one hand, to introduce some degree of porosity, thus accounting for volume expansion of lithiated silicon and, on the other hand, to address the need for overall mechanical integrity. In addition, the anisotropic, columnar structure could in principle promote faster kinetics and more effective electronic transport.
throughout the whole electrode thickness as well as hinder the segregation of particles during electrochemical operation.

An estimate of the densities of these films is provided in a previous work, with a value of 0.36 g cm$^{-3}$ for the sample 100 Pa, 0.92 g cm$^{-3}$ for 60 Pa and 1.66 g cm$^{-3}$ for 40 Pa. If compared to the density of bulk silicon (i.e., 2.33 g cm$^{-3}$), these result in estimated porosities of about 85, 60 and 29 %, respectively.

Accurate determination of specific surface area (SSA) in porous Si is usually performed through BET technique, which analyses the adsorption/desorption isotherms of gases at low temperature. Nitrogen adsorption-desorption isotherms, shown in Figure 2 (a-c), are mainly classified as type IV isotherms with a hysteresis loop. This type of isotherm denotes a mesoporous material (pore diameters of 2–50 nm) with the hysteresis loop being associated with the capillary condensation of nitrogen within the mesopores. In details, the relative pressure at which the hysteresis of adsorption/desorption is recorded in the isothermal profiles may account for the different pore size distribution in films having different morphology. By comparing BET data of Figure 2 with FESEM images shown in Fig. 1, two orders of porosity can be traced in each of the three films. The “first-order” porosity is the one given by large intra-algae pores with diameter size in the range of tens of nanometers and gives rise to the hysteresis in the low partial pressure range of the isotherms. The “second order” porosity is instead the one of voids between clusters composing each single alga of the film; these have a diameter in the range up to tens of nanometers and are represented by the hysteresis in the high partial pressure range of the isothermal profile. In sample 40Pa, the “first order” porosity dominates the overall
porosity, as from the position of the hysteresis in the isothermal profile as well as visually confirmed by FESEM analysis.

Figure 2 Isothermal profiles of single-layered Si films prepared at increasingly higher applied deposition pressures: (a) 40Pa, (b) 60Pa, (c) 100Pa.

On the contrary, the “second” order porosity becomes more important in films produced at higher pressure. As a consequence, the hysteresis in the isotherms shifts towards the range of higher partial pressures; this is particularly evident in sample Si-100, where almost only the “second” order porosity is present. Exploiting the BET theory, the
following values of specific surface area were obtained for each sample prepared varying
the deposition pressure: 68, 109 and 189 m² g⁻¹ for sample Si-40, Si-60 and Si-100,
respectively. As expected, surface area values increase almost linearly with the increase
in the applied deposition pressure from 40 to 100 Pa, in good agreement with SEM
analysis and with previous literature on porous films of silicon or other materials
prepared by PLD.²³,²⁴

Raman analysis on the as-prepared single-layered Si nanostructured anodes before
electrochemical tests reveals the amorphous character of their structure (see Fig. 3, where
only the Raman spectrum of sample 40Pa is shown as representative for the three
samples prepared), as from the characteristic Gaussian bands centred around 145, 330,
430 and 490 cm⁻¹ that are generally attributed to the transverse acoustic (TA),
longitudinal acoustic (LA), longitudinal optic (LO) and transverse optic (TO) modes of
amorphous Si, respectively.²⁵

**Figure 3** Raman spectrum of Si-40 (thick line), fitted by the characteristic Gaussian
curves of amorphous silicon (thin lines).
In samples produced at 100 Pa, an additional peak at 515 cm$^{-1}$ was detected, being attributed to the transverse optic (TO) mode of silicon crystals of nanometric size, in agreement with the literature$^{26-28}$ and with the capability, demonstrated in previous works, to grow Si nanocrystals by PLD (2.5 to 6 nm), embedded in an amorphous matrix$^{20}$. The ambient temperature electrochemical behaviour was evaluated in laboratory-scale lithium test cells and carried out by means of cyclic voltammetry and galvanostatic discharge/charge cycling at various current regimes. Results are shown in the plots of Figure 4 (a-c). Note that the electrodes were used as-grown on the Cu current collector, without any addition of binders and/or conducting additives.

The typical cyclic voltammetric response of the porous silicon nanostructures prepared by PLD is shown in Figure 4 (a) in its initial 10 cycles. Sample deposited at 40 Pa is representative for the complete set of samples here prepared. It was performed at the scan rate of 0.1 mV s$^{-1}$ between 0.02 and 1.5 V vs. Li$^+$/Li. The cyclic voltammograms (CV) show the typical behaviour of silicon electrodes upon reversible alloying/dealloying reactions with lithium ions,$^{29,30}$ resulting in two main couples of anodic and cathodic peaks. In details, in the initial scan towards lower potential values, it shows two cathodic peaks at below 0.2 V vs. Li$^+$/Li (i.e., around 0.15 V as the dominant, and around 0.05 V), characteristics of the lithiation step into amorphous silicon. These are reflected in the following anodic scan, where the two corresponding broad anodic peaks, centred at about 0.3 V and 0.47 V vs. Li$^+$/Li, indicate a two-step lithium extraction process from the Li–Si alloy back to amorphous Si. In the second cathodic scan, the broad cathodic peaks slightly shift towards higher potential values (e.g., the dominant centred at ca. 0.18 V). It is supposed to come from a slightly different kinetics in the alloying process due to the
formation of slightly different metastable amorphous Li$_x$Si phases according to the previous literature$^{31}$.

**Figure 4** Ambient temperature electrochemical behaviour in lab-scale lithium test cells of as-grown mesoporous single-layered Si nanostructures: (a) cyclic voltammetry (cycles 1-10) of sample 40Pa in the potential range of 0.02–1.5 V vs. Li$^+$/Li at a scan rate of 0.1 mV s$^{-1}$, (b) galvanostatic discharge/charge potential vs. specific capacity profiles of sample 40Pa at 130 µA cm$^{-2}$, (c) specific capacity vs. cycle number of the three samples. Moreover, in (d) the Raman spectra taken on Si-40 and Si-60 anodes after electrochemical tests are shown (together with the large band of amorphous silicon, the peaks of Li$_2$CO$_3$ are highlighted).

Regarding the formation of the solid electrolyte interphase (SEI) layer, it appears in the first cathodic scan as a broad faint signal between 0.6 and 0.4 V vs. Li. 
The potential vs. time profiles upon discharge (lithiation) and charge (delithiation) for sample 40 Pa, are shown in plot (b) of Figure 4. The charge/dischARGE current rate used for each sample was 0.1 mA, corresponding to about 130 μA cm$^{-2}$. Profiles show the typical features of amorphous silicon electrodes, with an initial discharge cycle being rather different from the following ones due to the formation of the SEI layer and to the presence of high oxygen content at the surface of the electrode, as usual for amorphous silicon nanoparticles. This causes the relatively large irreversible capacity loss, which always results in low initial Coulombic efficiency for these kind of electrode materials.

The cycling performance of the mesoporous single-layered Si nanostructures in lab-scale lithium test cells is shown in Figure 4(c). The initial 30 galvanostatic cycles account for good initial capacity higher than 200 μAh cm$^{-2}$ for all of the three porous films, with a capacity loss of about 40 % for sample 40 Pa and 50 % for both 60 Pa and 100 Pa upon initial lithiation; this is a reasonably low value for initial capacity decay if compared to similar high-surface-area silicon nanostructures reported in the literature$^{30}$. Based on the kind of synthesis adopted in the present work, the sample having lower surface area available for reaction with the electrolyte, i.e. the one prepared at a pressure of 40 Pa, shows in fact lower capacity loss during initial lithiation. This is reflected also in the overall electrochemical behaviour, which is superior both in terms of higher specific capacity values and stability upon reversible cycling, and results in the highest value of capacity retention (around 77 %) after 30 discharge/charge cycles in lithium cell.

After electrochemical tests, some of the cells were opened to characterize their status after-cycling. Representative Raman spectra of the anodes were acquired after their washing in EC:DEC in order to remove residuals from the electrolyte as well as glass-
fibres from the separator. In addition to the bands of amorphous silicon, the spectra reveal on all of the samples the presence of intense and sharp peaks at 96, 127, 156, 193, 273 cm$^{-1}$ that constitute the fingerprint of lithium carbonate (Li$_2$CO$_3$). As reported in several studies in the literature, Li$_2$CO$_3$ comes from the electrolyte decomposition in those systems that use LiPF$_6$ as the salt dissolved $^{24-27}$.

**Multi-layered Si/C bi-component films**

In order to improve the cycling performance of the newly elaborated silicon nanostructures, the sample having the most promising prospects in terms of galvanostatic cycling, namely Si-40, was successively prepared in the form of a multi-layered nanocomposite film where Si-40 layers were alternated to C ones. In this way, multi-layered structures were grown where Si and C were alternated 9 times (10 layers, 5 couples Si-C), starting with Si in contact with the copper collector and terminating with C on top of the whole stack. The role of the C top layer is to promote the formation of a stable SEI being in direct contact with the electrolyte, while the C layers in between of the stack are meant to improve the overall electrical conductivity and buffer the volume expansion of the Si layers. The multi-layered sample was then annealed at 400 °C for 5 minutes in inert atmosphere. The annealing treatment is thought to be effective for internal stress relaxation and is supposed to improve the adhesion of the Si film onto the copper substrate.
Figure 5 (a,b) Cross-sectional views at different magnification and (c) Raman spectrum of the multi-layered Si/C-40 film.

Cross-sectional views of the multi-layered Si/C-40Pa film acquired at different magnifications are shown in Figure 5(a,b). The alternated Si and C stacks are clearly visible for this sample, where silicon was grown at 40Pa, unlike the more porous samples with Si deposited at higher pressures (not shown here). Probably, the higher porosity of the single Si layer provides a rough surface for the deposition of C, which can then infiltrate into Si instead of forming a separate layer.
Raman investigation on multilayered samples is discussed upon considering the spectral
range as divided into two parts: the one containing the features arising from Si layers
(100-600 cm\(^{-1}\)), the other one accounting for C layers (1000-1800 cm\(^{-1}\)). In the range
100-600 cm\(^{-1}\) (left-hand side of the spectrum in Figure 5c), Raman spectra recorded on
as-deposited samples show the characteristic features of amorphous Si, i.e. the bands
related to the transverse acoustic (TA), longitudinal acoustic (LA), longitudinal optic
(LO) and transverse optic (TO) modes\(^{25}\), respectively, as in the case of single-layered
samples. For multilayered samples, the spectral region between 1000 and 1800 cm\(^{-1}\) was
also considered, and the spectra were fitted with four Gaussian curves, following the
procedure described by Ferrari et al.\(^{36}\). The right-hand side of the spectrum in Figure 5(c)
features the two typical bands of amorphous graphitic carbon, the one intense and broad
around 1330 cm\(^{-1}\) (D band) and the narrower one around 1540 cm\(^{-1}\) (G band), this latter
being associated to the in-plane stretching of \(sp^2\) bonds. D band, instead, arises from the
breathing mode of C-rings in disordered layers, e.g. from distorted 6-folded rings or from
rings of different order\(^{36,37}\).

Van der Pauw measurements were performed on the multi-layered Si/C-40Pa sample
either annealed or not, in order to estimate the film conductivity in the two cases. As
summarized in Table 1, the annealed samples show a 10-times smaller resistivity with
respect to the non-annealed ones. It is not straightforward to extract a value of
conductivity from these measurements, due to the inhomogeneous structure of the film
(i.e., a nanostructured nanoporous assembly) and, hence, the resistivity and conductivity
should be considered as effective quantities, viz. obtained by considering the film as
composed by an effective uniform 1µm-thick medium.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Eff. Resistivity (Ω cm)</th>
<th>Eff. Conductivity (Ω cm)^−1</th>
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<tbody>
<tr>
<td>Si/C-40 annealed</td>
<td>1.37E+03</td>
<td>7.29E-04</td>
</tr>
<tr>
<td>Si/C-40 not annealed</td>
<td>1.33E+04</td>
<td>7.51E-05</td>
</tr>
</tbody>
</table>

Table 1. Van der Pauw measurements on multi-layered Si/C-40, annealed and not-annealed.

The annealed multi-layered Si/C-40 nanocomposite film was then tested under the same constant current conditions as for the single-layered samples (i.e., 0.1 mA, viz. about 130 µA cm⁻²) between 0.02 V and 1.5 V (vs. Li⁺/Li). The cycling response at ambient temperature is shown in Figure 6, where both the charge/discharge potential vs. specific capacity profiles (graph a) and specific capacity vs. cycle number along with Coulombic efficiency (graph b) are plotted. In general, annealed samples showed good cyclability. The initial capacity of about 400 µAh cm⁻² is lost at only 15 % during the first cycle and then rapidly stabilizes slightly above 300 µAh cm⁻² in the following cycles. Noteworthy, the specific capacity exceeds 295 µAh cm⁻² after prolonged operation of 100 discharge/charge cycles. Clearly, if compared to the corresponding single-layered Si sample shown in Fig. 4, both a noticeable increase in the overall specific capacity as well as a profound improvement in the stability upon prolonged cycling was successfully obtained. Also the Coulombic efficiency rapidly reaches 99 % after the initial cycles and then stabilizes. It is noteworthy that galvanostatic charge/discharge curves of the reference samples (not annealed) were affected by a sudden drop in capacity during the initial cycles, with rapid cell failure. Thus, as expected, the annealing step proved to be
beneficial for the stability of the anodes, confirming the explanations provided in the literature about CVD-induced effects. Moreover, the role of the top layer of carbon in promoting the formation of a stable SEI is confirmed by the much more limited specific capacity loss upon initial lithiation (below 15%), if compared to the much more pronounced irreversible capacity loss exceeding 40% demonstrated by the corresponding mesoporous single-component Si film.

Figure 6 Ambient temperature galvanostatic cycling behaviour of the annealed multi-layered Si/C-40 nanocomposite film at 130 µA cm\(^{-2}\): (a) representative constant current discharge/charge potential vs. specific capacity profiles (100\(^{th}\) cycle), (b) specific capacity vs. cycle number along with Coulombic efficiency.

The results obtained clearly indicate that the multi-layered bi-component Si/C films prepared by sequential PLD deposition at 40Pa and successively annealed at 400 °C own a great potential to be used as a high capacity, highly stable anode material in the next-generation of lithium-based (micro)batteries.
Conclusions

Silicon is very attractive as active material for Li-ion battery anodes due to its high theoretical capacity, but proper nanostructuration is needed to accommodate the large volume expansion/shrinkage upon reversible cycling. This would overcome the disgregation induced by the lithiation/delithiation processes, often resulting in poor long-term performance.

In this work, mesoporous nanostructured silicon anodes were fabricated by Pulsed Laser Deposition technique, characterised and electrochemically tested in lab-scale lithium test cells. Different deposition pressures were exploited in order to evaluate the influence of this process parameter on the morphological/electrochemical characteristics of the resulting nanostructures. The sample prepared at lower deposition pressure, having porosity featured by larger average pore size and lower surface area, showed initial capacity approaching 250 µAh cm\(^{-2}\) upon 30 galvanostatic discharge/charge cycles. We believe that the higher stability of the samples deposited at lower pressure can be related to their lower surface area. On the contrary, the higher surface area of the more porous samples (samples 60 Pa and 100 Pa) is likely to be responsible for their increased capacity fade; more surface area is involved, in fact, in the side reactions with the electrolyte and, hence, more capacity is lost in forming the interphase layer. The appearance of intense peaks attributed to Li\(_2\)CO\(_3\) in the Raman spectra confirms that losses due to the SEI formation are relevant to the proper operation of the single-layered films.

Moreover, alternated deposition of Si/C layers by PLD has proven to be a straightforward method to produce multi-layered bi-component electrode films in one processing step.
The addition of carbon and mild annealing at 400 °C stabilized the electrochemical performance in lithium cells: compared to the corresponding single-layered Si sample, both a noticeable increase in the overall specific capacity as well as a very profoundly improved stability upon prolonged cycling has been successfully obtained. The beneficial impact of an increased conductivity upon annealing may have a role in the improved electrochemical performances of the annealed silicon anodes, as it can promote faster kinetics in lithiation-delithiation.

Thus, engineering voids at the nanoscale, by direct introduction of specific porosity during growth and producing alternated Si and C multi-layered nanocomposite films, opens up the route for the effective use of silicon as lithium battery anode without the need for any binder or conductive additive that would lower the overall energy density of the resulting device. Further developments of this work shall include a thorough study of the effects of annealing at lower temperatures, in view of larger scale applicability. This would lead to a definition of an optimum temperature, i.e. the minimum one for the stabilizing effect to occur, and provide useful information for the successive integration of the annealing step into the deposition process, by means of a heated sample-holder. This would further reduce fabrication steps, making it possible to deposit and anneal silicon and carbon in one single processing step.

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