



## Review article

# Advances in physical vapor deposited silicon/carbon based anode materials for Li-ion batteries

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## ABSTRACT

This paper explores the latest developments in physical vapor deposition (PVD) techniques for fabricating silicon-carbon (Si/C) based thin films as anodes of Lithium-Ion batteries (LiBs). Properties of Si/C based materials, such as high thermal stability, electrical conductivity and mechanical strength, have addressed the critical challenges associated with the use silicon as anode material for LiBs, including as volume expansion during lithiation, structural stability and electrode degradation.

The review article aims to provide recent advances in the use of Si/C-based thin film materials deposited via PVD processes as anodes for LiBs. PVD deposition processes provide numerous benefits including the precise control over the structure, thickness, morphology, as well as the design of deposited thin-film materials, and this article provides an in-depth analysis on the design and synthesis of Si/C thin films, as well as its electrochemical performance and stability when used as anode for LiBs.

The primary aim of this paper is to underscore the advantages provided by PVD processes in overcoming challenges associated with using pure silicon as anode material for LiBs, or in improving the electrochemical performance of Si/C-based anode materials through the design of several Si/C films, covering both multilayer and nanocomposite Si/C film configurations outlined in sections 2 and 3, respectively. Insights into the mechanisms governing lithium-ion insertion/extraction processes within the Si/C matrix are provided, offering an understanding of the material's behavior during battery cycling.

## 1. Introduction

Secondary batteries, commonly referred to as rechargeable batteries, have significantly transformed energy storage technology and are widely investigate and utilized across diverse domains such as mobile devices, energy storage systems, and hybrid electric vehicles [1–5]. These batteries necessitate to meet specific performance requirements like high energy density, cyclability, cost-effectiveness, and safety [6–8]. Lithium-ion batteries (LiBs) are leading the way in research as the most extensively studied energy storage systems for mobile applications. Nonetheless, ongoing research efforts in battery materials, design, and manufacturing processes aim to enhance their performance, stability, and safety [9,10].

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Among the materials explored, silicon stands out as a promising candidate due to its high theoretical capacity (ca. 4200 mAhg<sup>-1</sup>) and low discharge potential (0.06 V vs. Li/Li<sup>+</sup>) [11,12]. However, the practical implementation of silicon anodes faces significant challenges related to their large volume expansion during lithiation, leading to mechanical stress and electrode degradation. Furthermore, the instability of the solid-electrolyte interphase (SEI) during cycling result in continues active material consumption and a persistent decrease in the coulombic efficiency [13,14]. In addition, the low mechanical stability and chemical passivation properties make the cyclability of silicon electrodes far from being able to meet the requirements of battery systems [8,15].

To address these challenges, it has been suggested combining Silicon with other materials to enhance electrochemical performance, materials like SiCu [16], SiAg [17] and NiSi [18] have demonstrated considerable capacity along with good capacity retention. However, Si/C based electrode materials have emerged as a significant area of interest in the development of high-performance LIBs [15,19] [-] [21]. The properties of the Si/C materials contributed to addressing key challenges associated with traditional electrode materials, particularly those made of silicon. The use of Si/C characterized by high mechanical properties and thermal conductivity, contributes to improved structural stability, enhanced electrical conductivity, and increased cyclability, paving the way for the development of high-performance and long-lasting anode material for LIBs [22–24]. On the other hand, the versatility of silicon-carbon enables its integration into various electrode designs [24,25], this flexibility allows for the exploration of various approaches to optimize performance based on specific application requirements.

In recent years, physical vapor deposition (PVD) of silicon-based materials has emerged as a compelling technique to address the specific challenges associated with conventional Silicon-based electrode fabrication methods [26,27]. PVD techniques, such as sputtering and evaporation, offer precise control over film uniformity and thickness, resulting in thin, uniform layers of silicon on current collectors. In addition, PVD techniques can be readily scaled for mass production, with reproducible processes that ensure consistent quality in large-scale manufacturing. PVD technologies also allows improves the manufacturing process for batteries, including engineering of complex and tailored electrode architectures with improved adhesion and degradation resistance [28].

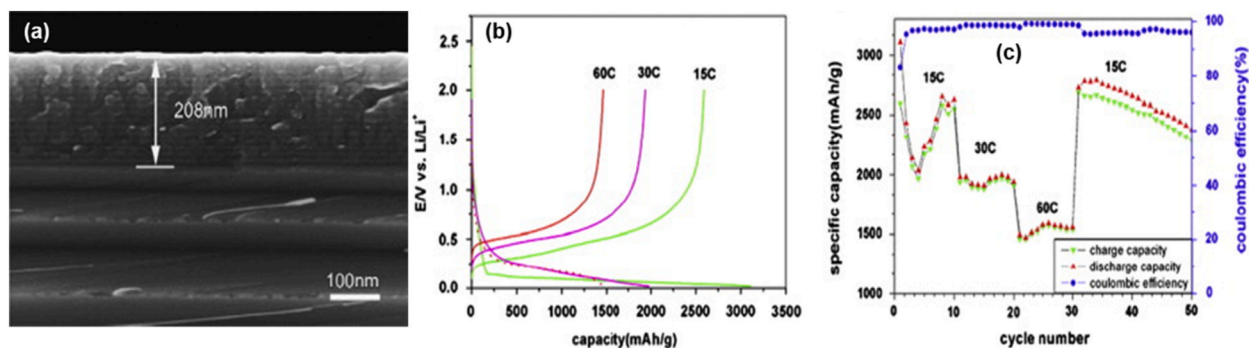
Furthermore, conventional electrode fabrication involves the use of binders and conductive additives to hold active materials together and improve electrical conductivity [29,30]. The inclusion of these components can, however, hinder the performance of the electrode, by decreasing the reaction area and increasing the ion transport resistance [31]. PVD deposited electrodes eliminate the need for binders and conductive additives, leading to a more direct interaction between the active material and the current collector, thereby enhancing overall conductivity and reducing the electrode manufacturing cost [24,32].

This review article aims to provide an overview of the application of physical vapor-deposited Si/C based materials as an anode material in lithium-ion batteries. Discussions are mainly focused on structure design, synthesis methods and electrochemical performance and stability.

## 2. Multilayered Si/C as anode materials for LiBs

Numerous investigations have illustrated that employing vacuum physical deposition to fabricate Si/C multi-layered films, consisted of several repetition of Si and C layers, is an effective approach for developing lithium-ion battery electrodes characterized by both high specific capacity and prolonged cycle stability. In these configurations, the silicon and carbon layers are fabricated using either direct current magnetron sputtering (DcMS) [22,23] or radio frequency magnetron sputtering (RfMS) [25,33], or through distinct approaches where silicon is deposited via RfMS and carbon is deposited via DcMS [24,25,27,34,35]. Carbon layer is commonly used as a first layer in the Si/C multi-layered films, which helps to get a relatively better adhesion.

Yi Zhao et al. [23] utilized DcMS to produce Si/C multilayer films (500 nm thick). The incorporation of a carbon layer as a buffer for silicon volume expansion effectively prevented film cracking during lithiation/delithiation process and prevent the direct contact of silicon with the organic electrolyte. Using multilayer Si/C electrodes, the Li-ions diffusion kinetics are promoted along the directions that are perpendicular to the Si–C interfaces. The optimal electrochemical performance was achieved with a Si (15 nm)/C (5 nm) multilayer film anode, exhibiting an initial discharge capacity of 2640 mAh g<sup>-1</sup> and a charge capacity of 2560 mAh g<sup>-1</sup>. The electrode demonstrated an initial coulomb efficiency of 97 % and maintained a capacity retention of 87 % after 200 cycles. Likewise, Jun Wang



**Fig. 1.** (a) SEM of the structure of the Si/C multilayer thin film. (b) The charge–discharge curve of 1st (15C), 11th (30C) and 21st (60C) cycles. (c) The capacity at various rates from 15C to 60C. Reproduced with permission [25]. Copyright 2013, Elsevier.

**Table 1**

Overview of the structure and electrochemical performance of different Si/C thin film electrodes fabricated by PVD.

Anode Material	Structure	Deposition Method	Initial Discharge Specific Capacity (mAh/g)	Initial Charge Specific Capacity (mAh/g)	Initial Coulombic Efficiency (%)	Capacity Retention	Ref.
<b>Si/C Multilayer</b>	Si (5 nm)/C(2.5nm/ ... /Si (5 nm)/C(7 nm) – overall thickness: 400 nm	DcMS	2532	2210	87.3	1612 mAhg <sup>-1</sup> in 200 cycles	[22]
	Si (10 nm)/C(5nm/ ... /Si (10 nm)/C(7 nm) – overall thickness about 400 nm	DcMS	2673	2342	87.6	2729 mAhg <sup>-1</sup> in 200 cycles	[22]
	Si (15 nm)/C(7.5nm/ ... /Si (15 nm)/C(7 nm) – overall thickness about 400 nm	DcMS	2449	2147	87.7	2122 mAhg <sup>-1</sup> in 200 cycles	[22]
	Thickness ratio Si:C of 5:1	RF magnetic sputtering	3107	2592	83 %	99 %: 2000 mAhg <sup>-1</sup> at 30C, 1500 mAhg <sup>-1</sup> in 60C	[25]
	Si (20 nm)/C (5 nm), overall thickness 500 nm	DcMS	2940	2800	95 %	2300 mAhg <sup>-1</sup> in 200 cycles	[23]
	Si (15 nm)/C (5 nm), overall thickness 500 nm	DcMS	2640	2650	97 %	2300 mAhg <sup>-1</sup> in 200 cycles	[23]
	Si/C/Si (70/5/70 nm)	Si (RfMS), C (DcMS)	–	–	50 ± 4 % and 87 ± 6 % for 1st & 2nd cycles	87 ± 1 in 150th cycle	[35]
	Si/C/Si (70/10/70 nm)	Si (RfMS), C (DcMS)	–	–	54 ± 4 % and 88 ± 6 % for 1st & 2nd cycles	82 ± 2 % in 150th cycle	[35]
	Si/C/Si (70/50/70 nm)	Si (RfMS), C (DcMS)	–	–	61 ± 1 % and 88 ± 2 % for 1st & 2nd cycles	83 ± 6 in 150th cycle	[35]
	Si/C/Si (100/20/100 nm)	Si (RfMS), C (DcMS)	2092.67	–	65.70 %	83.46 % in 150 cycles	[34]
	Si/C/Si/C/Si/C/Si (50/10/50/10/50/10/50 nm)	Si (RfMS), C (DcMS)	1888.74	–	67.45 %	96.82 % in 150 cycles	[34]
	*C/Si (20/100 nm)	Si (RfMS), C (DcMS)	2087.8	–	67.2 %	82.0 % in 200 cycles	[24]
	*Si/C/Si (50/20/50 nm)	Si (RfMS), C (DcMS)	2119.3	–	66.6 %	73.7 % in 200 cycles	[24]
	*C/Si/C/Si (10/50/10/50 nm).	Si (RfMS), C (DcMS)	2045.9	–	68.0 %	99.2 % in 200 cycles	[24]
	a-C/Si(~50/~250 nm)	Si and C (RfMS)	~3086	~2509	~99.5 % up to 50 cycles	Fade in capacity of ~0.02 % loss per cycle, up to 50 cycles. Then 0.2 % loss per cycle after 50 cycles.	[33]
a-C/Si(~50/~250/~50 nm)	Si and C (RfMS)	~2531	~2025	~99.5 % up to 50 cycles	Fade in capacity of ~0.03 % loss per cycle, up to 50 cycles. Then 0.14 % loss per cycle after 50 cycles.	[33]	
Graphite/Si (1 μm)	Silicon deposited by HiPIMS	628.7	510.6	81 %	96 % in 140 cycles	[19]	
<b>Si/C nanocomposite</b>	Si <sub>51</sub> C <sub>49</sub>	RfMS	2000	–	–	58 % after 200 cycles	[44]
	Si <sub>45</sub> C <sub>55</sub>	RfMS	2190	–	–	55 % in 200 cycles	[44]
	Si <sub>37</sub> C <sub>63</sub>	RfMS	2690	–	–	56 % in 200 cycles	[44]
	Si/MWCNT	50 nm of Silicon deposited by RfMS	2435	–	22 %	600 mAhg <sup>-1</sup> in 100 cycles	[45]
	Si/MWCNT	130 nm of Silicon deposited by RfMS	2100	–	18 %	1250 mAhg <sup>-1</sup> in 100 cycles	[45]

et al. [22] demonstrated the stability of the SEI in the amorphous Si (10 nm)/C (5 nm) multilayer electrode compared to pure silicon. The carbon layer plays a role in relieving stress concentration induced by volume expansion during the lithiation/delithiation of silicon. The specific capacity reached  $2729 \text{ mAh g}^{-1}$ , surpassing the theoretical capacity, and remained stable over 200 cycles. This accomplishment was attributed to enhanced Li-ion transport within the multilayered Si/C anode, linked to the polarization of the  $\text{Li}_x\text{Si}$  alloy and the presence of defects at the Si-C interfaces.

Wang and colleagues fabricated Si/C multilayer electrodes by RfMS, with a total thickness of approximately 208 nm and a modulation period of 20 nm (Fig. 1a) [25]. In addition to the carbon layers restraining the volume expansion of the silicon layers, it was claimed that the presence of defects in the amorphous Si/C layers deposited provide pathways for lithium diffusion, which helped in diminishing the irreversible discoloration of the capacity. The electrode exhibited a high initial capacity of  $3107 \text{ mAh g}^{-1}$  with a Coulombic efficiency of 83 %. The films retained a substantial capacity of  $1500 \text{ mAh g}^{-1}$  even at a high charge-discharge rate of 60C (Fig. 1b and c) while maintaining a high coulombic efficiency. Same role of adding amorphous carbon (C) layer as either surface layer (C/Si) or interlayer (Si/C/Si) anodes have been reported by Antonia Reyes et al. [35].

Similarly, other studies have shown that introducing a carbon film, deposited through the DcMS method, either as a surface layer or an interlayer in Si/C multilayer electrodes, where Si is deposited using RfMS, significantly enhances both cycling stability and conductivity when compared to pure silicon [24,25,27,34,35]. Table 1 summarizes the electrochemical performances of the batteries. Tong et al. prepared Si/C multilayer films in several configuration (Fig. 2a-d) [24]. It was shown that the Si/C multilayered electrodes

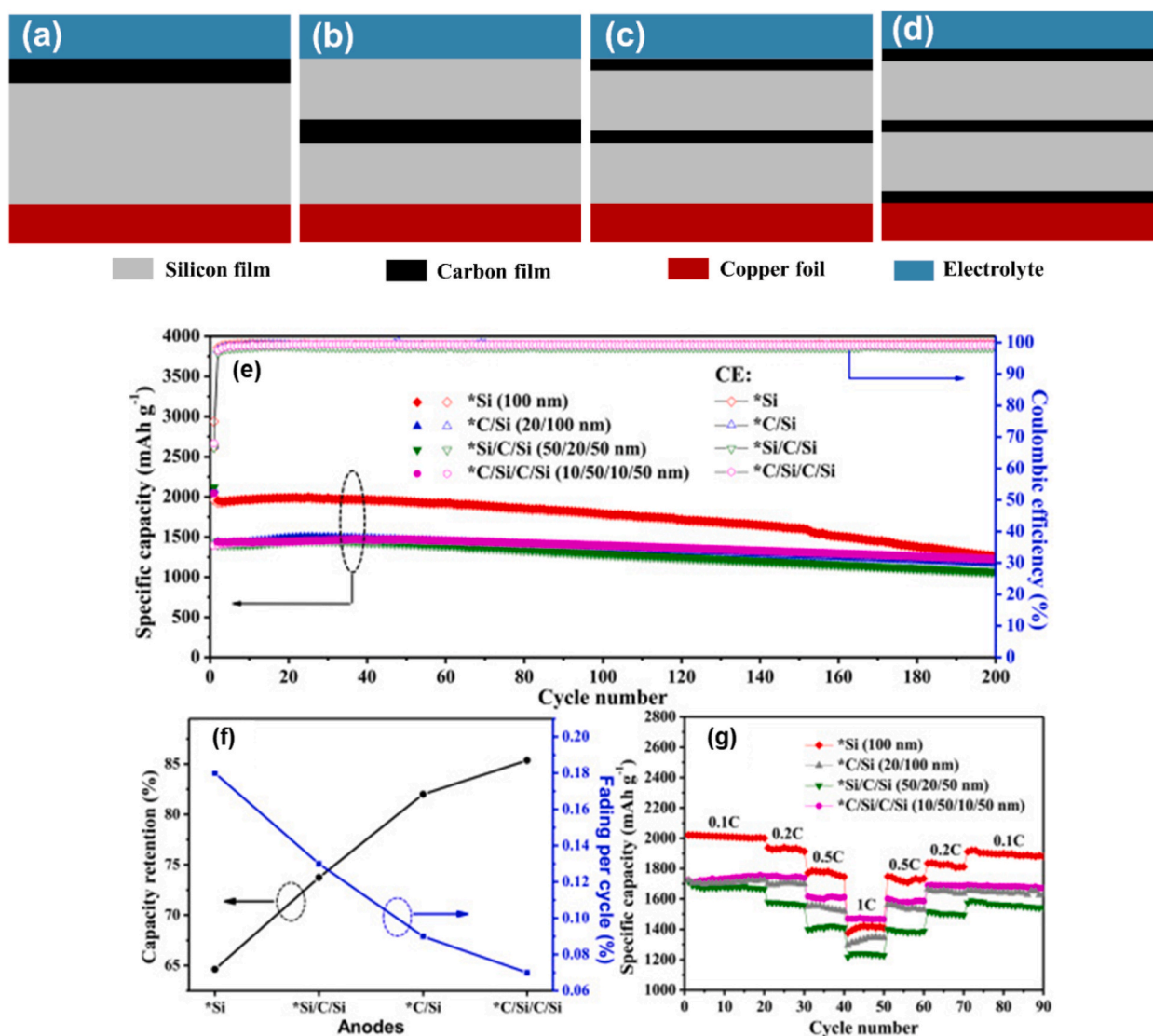


Fig. 2. Schematic illustration of the electrode models of: (a) \*C/Si (20/100 nm), (b) \*Si/C/Si (50/20/50 nm), (c) \*C/Si/C/Si (10/50/10/50 nm) and (d) \*C/Si/C/Si/C/Si (10/50/10/50/10 nm) anodes. (e) Cycling performance and Coulombic efficiency (CE), (f) capacity retention and fading per cycle, and (g) rate capability of different Si/C multilayer film electrodes. Reprinted with permission [24], Copyright 2019, Elsevier.

exhibited high higher specific capacity, cycling stability and rate capability (Fig. 2e–g), thanks to the embedded amorphous carbon layer which controls the volume expansion, while the formation of the  $\text{Li}_x\text{C}_y$  alloys passivate the film, maintaining structural integrity during lithium uptake/extraction [24]. Additionally, introducing an extra carbon film on the Si or Si/C electrodes further enhances cycling stability, charge resistance by enhancing electronic conductivity at the electrode-electrolyte interface, and protects the highly reactive Si surface from the electrolyte [34,35].

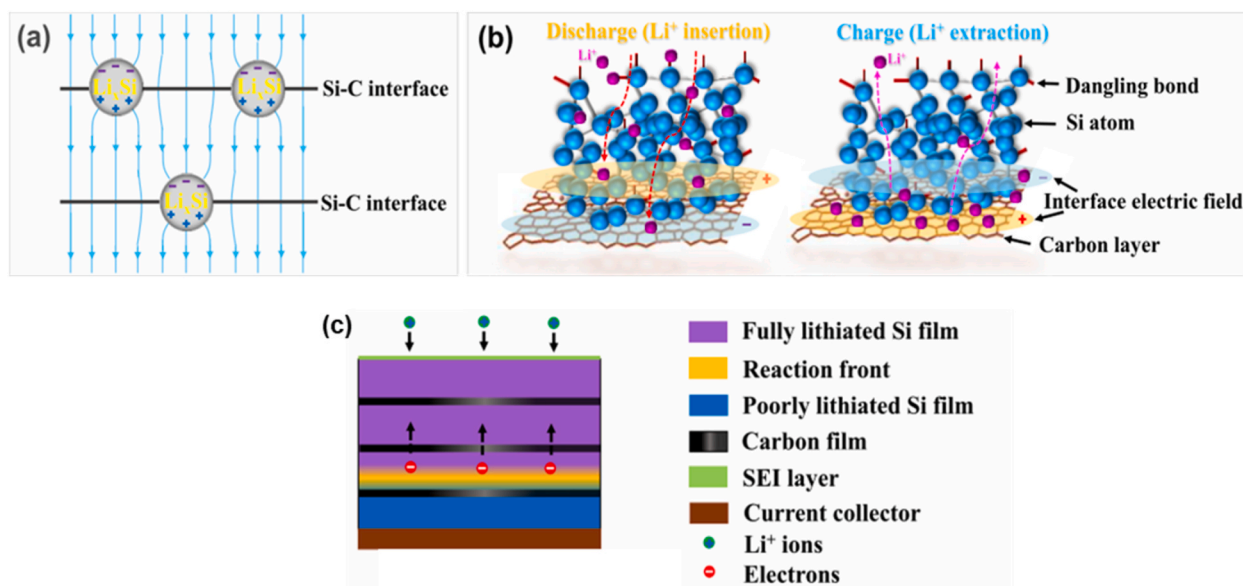
Ion-Beam Sputtering deposition technology was employed for the fabrication of Silicon, Carbon, and Si/C Multilayers. The individual layer thicknesses for silicon and carbon were varied in the ranges of 5–27 nm and 14–230 nm, respectively [36]. Consistent with prior findings, the combination of silicon and carbon demonstrated enhanced capacity and cycling stability when compared to single silicon and carbon films. This improvement can be attributed to the synergistic benefits derived from the reversible cycling of carbon combined with the high-capacity characteristics of silicon. The study also concluded that employing thicker silicon films contributes to attaining higher capacities. This is attributed to the increased quantity of incorporated lithium reaching the thresholds of  $x = 3.70$ , necessary to initiate the crystallization process of the amorphous  $\text{Li}_x\text{Si}$  phase [37,38].

Ling Tong et al. provided a possible mechanism to comprehend the effect of interface engineering on the electrochemical performance and stability of Si/C multilayered electrodes for LIB applications [34]. One possible route is that the formation of the  $\text{Li}_x\text{Si}$  alloys which nucleate and grow at Si–C interfaces enhances local electric field [39], which result in the local polarization at the interfaces [40]. In a static electric field, conductive  $\text{Li}_x\text{Si}$  alloy spheres induce charge redistribution and local polarization near their surfaces (Fig. 3a). This creates a zero-electric field inside the spheres and a heightened local external field. Consequently, the locally coupled built-in electric field enhances  $\text{Li}^+$  ion diffusion within multi-layered Si/C film anodes [34]. An alternate mechanism suggests that ion diffusion and electron transfer are enhanced thanks to the presence of defects and dangling bonds, creating additional space and pathways for lithium ions within amorphous Si and carbon films (Fig. 3b) [34]. This could be combined with the locally induced in-plane electric field, resulted from either structural distortion and disorder at the heterogeneous interface [41], or an imbalanced distribution of Li ion concentration between Si and carbon layers during cycling [42]. Another mechanism, suggests that incorporating conductive carbon layers into Si/C anodes improves the overall electrical conductivity of Si-based anodes, lengthens the  $\text{Li}^+$  diffusion length, preserves structural integrity, and forms a stable SEI layer, preventing electrolyte penetration into the sandwiched structure (Fig. 3c) [43].

### 3. Nanocomposite Si/C as anode materials for LiBs

The nanocomposite and nanomaterials Si/C anode are usually prepared by several methods such as physical vapor deposition [44–46], chemical vapor deposition method [47–49], plasma spraying [50], Solid phase synthesis method [51], liquid phase synthesis method [52], some of them require high temperature treatment [53].

A limited number of studies have directed their attention towards the application of PVD methods in depositing Si/C nanocomposite films for use as anodes in LiBs. This limited attention could be explained by the challenges associated with synthesizing Si/C nanocomposites through PVD techniques, which hinder precise control over composition, morphology, and structure. Furthermore,



**Fig. 3.** (a) Schematic illustration of enhanced local electric field by the formation of  $\text{Li}_x\text{Si}$  alloys at Si–C interfaces. (b) Schematic illustration of the formed in-plane electric field and improved  $\text{Li}^+$  ion transport at Si–C interface during discharge and charge processes. (c) Schematic cross-sectional illustration of the lithiation process of multilayered Si/C anode at intermediate state. Reproduced from Ref. [34], Copyright (2020) American Chemical Society.

ensuring compatibility between silicon and carbon through PVD, while simultaneously preserving desired properties and performance in LIB applications, requires precise optimization of deposition parameters. This task demands a comprehensive understanding of both thin film growth and the electrochemical behavior of the Si/C nanocomposite anode, spanning across multiple disciplines.

Xinghua Chang et al. fabricated homogenous Si/C nanocomposites utilizing a tandem plasma reactor, consisted of a magnetron sputtering source with an inductively coupled plasma positioned coil between the target and the substrate [46]. It was shown that the incorporation of 10 wt% carbon in silicon enhances both capacity and cyclic stability. The anode delivered 2nd cycle capacity of 3032 mAh g<sup>-1</sup> with a capacity retention of 2100 mAh g<sup>-1</sup> after 200 cycles. Pure silicon, on the other hand, had a 2nd cycle capacity of 980 mAh g<sup>-1</sup>, which drops to 590 mAh g<sup>-1</sup> after 120 cycles. This success was related to the enhanced Li<sup>+</sup> transfer in the Si/C as well as electrodes' stability.

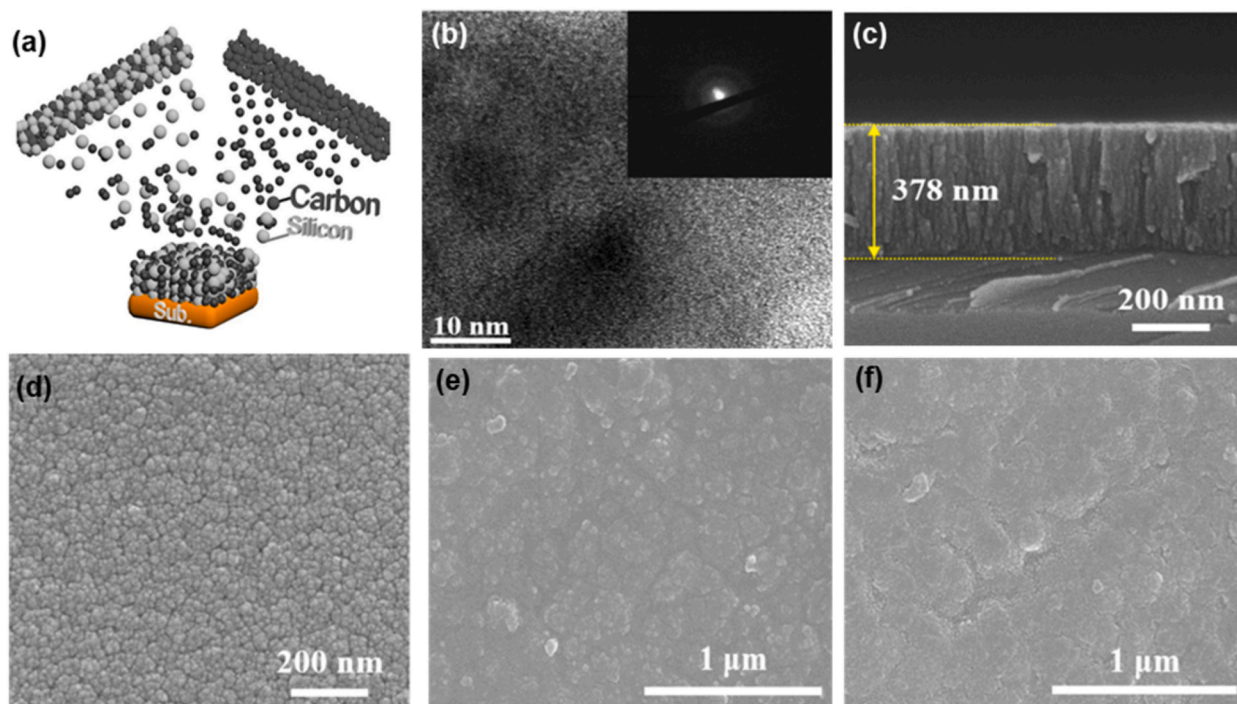
To explore the ideal amount of carbon to incorporate into silicon, K.S. Lee et al. deposited and examined the electrochemical performance of amorphous Si<sub>1-x</sub>C<sub>x</sub> with varying carbon contents (x) deposited by magnetron co-sputtering as shown in Fig. 4 [44]. The study revealed that the capacity retentions of Si<sub>1-x</sub>C<sub>x</sub>, increased with higher carbon content. A film with Si<sub>37</sub>C<sub>63</sub> composition exhibited a capacity of 1510 mAh g<sup>-1</sup> and maintained a capacity retention of approximately 96 % after 200 cycles. Furthermore, these films displayed good structural integrity without any signs of cracks or delamination, showing the positive buffering effect of carbon by reducing stresses resulted from volume expansion during long term cycling.

#### 4. Conclusion and perspective

In conclusion, this review underscores the pivotal role of PVD methods in shaping Si- based anode materials for lithium-ion batteries (LIBs). The exploration of PVD techniques has revealed their potential in addressing critical challenges associated with silicon anodes, elevating the performance and stability of LIBs. The controlled deposition of Si/C films through PVD not only mitigates issues of volume expansion and degradation but also opens avenues for enhanced electrical conductivity and extended cycle life.

The comprehensive analysis of various studies presented in this review establishes a clear link between PVD-deposited Si/C structures and improved specific capacities, cycling stability, and rate capabilities in LIBs, thanks to improved mechanical flexibility, high electronic conductivity and chemical stability in the electrolyte. It also shed light on the benefits driving the success of PVD Si/C anodes, mainly for in designing anodes materials with optimized electrochemical performance.

Although significant progress has been made in enhancing the electrochemical efficiency of Si/C thin film electrodes, numerous challenges persist, which require designing and developing stable multilayer and nanocomposite Si/C electrode materials as anode for LIBs. Tackling these obstacles paves the way for novel research avenues demanding interdisciplinary collaboration in the fields of materials science, electrochemistry, thin film growth and engineering. This collaboration is crucial for the advancement of high-



**Fig. 4.** (a) Illustration of co-sputtering system. (b) High resolution TEM, (c) cross section and (d) surface SEM images of the as deposited Si<sub>37</sub>C<sub>63</sub> thin film. SEM images of the Si<sub>37</sub>C<sub>63</sub> surface after (e) 5th cycle and (f) 200th cycle at a current density of 40 μA cm<sup>-2</sup>. Reproduced from Ref. [44], Copyright (2020), Elsevier.

performance and stable Si/C-based thin film batteries tailored for future energy storage needs.

One of the main obstacles stems from the expansion in volume that silicon-based electrodes undergo during cycling. This expansion results in mechanical deterioration, leading to electrode degradation and a decrease in battery capacity over time. In addressing these risks associated with Si/C-based thin film anodes, there is a need to develop electrode architectures through the utilization of physical vapor deposition (PVD) techniques. This includes focused effort to tune the anode configuration, silicon-to-carbon ratio, morphology and nano-structure of the Si/C thin films and meet the requirements for enhanced electrochemical characteristics.

Moreover, ensuring interface compatibility within the multilayer Si/C electrodes and with other battery components is crucial for maintaining long-term performance. Interfaces play a pivotal role in facilitating ion transport, electron conduction, and maintaining mechanical integrity. In addition, integrating Si/C based thin film electrodes with other battery components, including electrolytes and current collectors, represents a significant development direction. For instance, leveraging PVD methods for depositing protective films on electrodes can help mitigate issues such as electrode-electrolyte interfacial reactions and interfacial resistance, thereby addressing capacity fading and extending cycle life.

On the other hand, the challenge lies in attaining cost-effective deposition methods and scaling up production without compromising the quality of the Si/C based anode materials. Hence, there is a need to narrow the gap between laboratory-scale research and large-scale manufacturing by embracing PVD technologies for commercial LIBs. Nevertheless, the continuous progress in PVD technology, combined with enhanced control over the deposition process and a better comprehension of material interactions at the nanoscale, offers the potential to refine Si/C film structures for enhanced electrochemical performance. There is a need for further research to concentrate on refining PVD processes, fine-tuning deposition parameters, enhancing deposition rates, and developing cost-effective manufacturing techniques while preserving the integrity of Si/C thin films suitable for advanced battery applications.

By addressing these challenges and leveraging emerging technologies, the development of Si/C thin film anodes by PVD methods holds great promise for enhancing the energy density, cycle life, and safety of LIBs, thereby driving the widespread adoption of electric vehicles and grid-scale energy storage systems.

#### Data availability statement

Data will be made available on request.

#### CRedit authorship contribution statement

**Ghizlane El Omari:** Writing – review & editing, Data curation. **Khadija Elkindoussy:** Data curation, Formal analysis. **Mohamed Aqil:** Writing – review & editing. **Mouad Dahbi:** Writing – review & editing. **Jones Alami:** Writing – review & editing. **Mohammed Makha:** Writing – review & editing, Writing – original draft, Validation, Supervision, Funding acquisition, Data curation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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