

RESEARCH ARTICLE OPEN ACCESS

Operando Structural Rearrangement of Self-Ion-Implanted Germanium Films Enables High-Rate Cycling in Lithium-Ion Batteries

Valentina Diolaiti¹  | Alfredo Andreoli¹  | Silvio Fugattini² | Marco Ricci² | Shyamal Mondal^{3,4} | Damiano Giubertoni³ | Eleonora Venezia² | Mirko Prato² | Sergio Marras² | Silvia Dante² | Andrea Pegoretti^{3,5} | Rossana Dell'Anna³ | Remo Proietti Zaccaria² | Donato Vincenzi¹ 

¹Department of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy | ²Istituto Italiano di Tecnologia, Genova, Italy | ³Fondazione Bruno Kessler Sensors and Devices Center, Povo, Italy | ⁴Institut BioSens, Novi Sad, Serbia | ⁵Department of Physics, University of Trento, Trento, Italy

Correspondence: Marco Ricci (marco.ricci@iit.it)

Received: 14 October 2025 | **Revised:** 17 February 2026 | **Accepted:** 22 February 2026

Keywords: ion-implantation | lithium-ion battery | nanostructured germanium | negative electrode | plasma enhanced chemical | vapour deposition

ABSTRACT

Germanium (Ge) is a strong contender to produce negative electrodes for lithium-ion batteries. However, the drawbacks of Ge are well known: its volume changes dramatically during cycling, leading to low stability and efficiency. One way to mitigate this problem is to make the material porous, allowing it to accommodate the volume change. The porosity can simultaneously facilitate ion diffusion through the electrode, improving its performance. Ion implantation is an interesting method to produce porous films since it does not involve liquid-phase chemistry or active material removal. Moreover, it can be integrated with deposition techniques employed in the field of semiconductor processing, like plasma-enhanced chemical vapour deposition (PECVD). For these reasons, in this study, Ge negative electrodes for LIBs were produced as film by PECVD directly on the current collector (Molybdenum foil); then, they were made porous through ion implantation with Ge⁺ ions. Their performance (rate capability and stability) was tested through electrochemical cycling. These binder-free electrodes showed a remarkably stable specific capacity of 1360 mAh g⁻¹ for more than 400 galvanostatic cycles at a rate of C/4 and could provide a capacity of 490 mAh g⁻¹ and 280 mAh g⁻¹ at 40C and 60C, respectively. Notably, at high rates, the material undergoes structural changes that gradually enhance its high-current performance, demonstrating its suitability for high-power applications.

1 | Introduction

In the pursuit of new active materials to improve the energy density of lithium-ion batteries (LIBs), silicon (Si) and germanium (Ge) are promising candidates to produce negative electrodes. This is because the theoretical specific capacity of these materials –3579 mAh g⁻¹ for the formation of Li₁₅Si₄ and 1384 mAh g⁻¹ for the formation of Li₁₅Ge₄ – is well above that of graphite (372 mAh g⁻¹), the standard material used in commercial LIBs [1, 2]. Germanium, however, has an intrinsic conductivity four orders of magnitude higher than Si (2.1 S m⁻¹ vs 1.6 × 10⁻³ S m⁻¹)

[3] and 400 times higher Li⁺ diffusivity at room temperature, enabling faster electron and ion transport [4]. These features suggest that Ge might be superior to Si for high-power batteries, making the development of a stable Ge-based negative electrode an enticing prospect.

The feasibility of an electrode made of a pure Ge film was demonstrated by Graetz et al. [5]. Afterwards, researchers aimed to increase the stability and efficiency of Ge-based electrodes by manipulating the morphology of the active material: nanowires [6–9] and porous electrodes [10–12] are among the structures

Valentina Diolaiti, Alfredo Andreoli, Silvio Fugattini and Marco Ricci equally contributed to this study.

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2026 The Author(s). *physica status solidi (a)* applications and materials science published by Wiley-VCH GmbH.

most frequently reported in the literature, as also suggested by Sun et al. [13]. The reason is that these morphologies allow for better accommodation of the $\sim 300\%$ volume change that Ge experiences during cycling [14, 15] compared to a compact film. Furthermore, such electrodes have a higher surface area and shorter Li^+ diffusion pathways than bulk ones, usually leading to superior electrochemical performance. As an alternative to structuring the material during production, compact film electrodes can also be made porous after production [16]. Among the available processes for achieving porous films, electrochemical etching has been proposed in several instances [17, 18], including previous work by our group [19]. Another approach is ion implantation [20–22], which exploits a high dose of high-energy massive ions (with an atomic mass similar to or higher than the target) to bombard the film, as depicted in Figure 1.

In the case of Ge, the collision of the heavy ions with the film generates a peculiar honeycomb-like structure composed of tubular cavities [23–27]. This method offers several benefits compared to etching. First, it enables the production of porous films without requiring material removal or liquid-phase chemistry, thereby maximising atom economy and minimising waste. Additionally, the parameters of the ion beam, such as energy, ionic species and fluence, can be precisely adjusted to optimise the porosity and morphology of the structures to meet target requirements [28, 29]. Furthermore, as a well-established technique in the semiconductor industry [20], ion implantation can be seamlessly integrated with film deposition techniques routinely employed in the same field, such as plasma-enhanced chemical vapour deposition (PECVD) [30], to process wafer-scale (cm^2) samples.

For these reasons, in this work, we delved into the production and characterisation of Ge-based electrodes by using PECVD as the deposition method and combining it with ion implantation to create the porous structure. These production steps result in electrodes made of 100% active material (compared to $\sim 96\%$ for marketed electrodes [31]), maximising energy density. Ge ions were chosen as the incident species (so-called “self-ion implantation”^{–1}) [23] to avoid the introduction of impurities, which could modify the electrochemical response of the material.

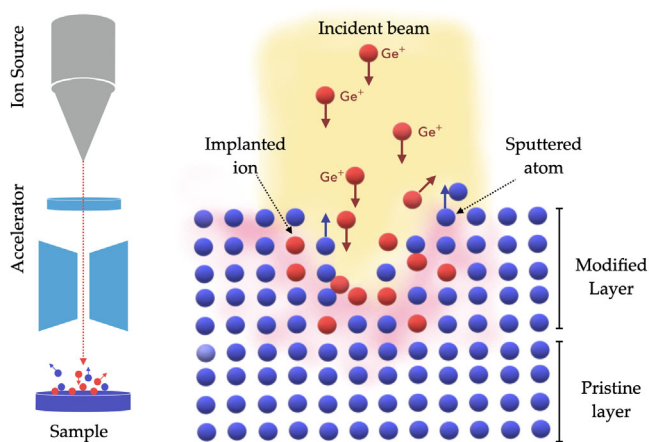


FIGURE 1 | Schematic of the nanostructuring process of the Ge-deposited layer via self-ion implantation.

The deposition and implantation process parameters were chosen to obtain samples of porosity and thickness close to the etched samples presented in our previous work [19, 32, 33] for the sake of comparability. The parameters for the ion implantation process have been selected after screening through the Monte Carlo-based stopping and range of ions in matter software package [34].

2 | Materials and Methods

2.1 | Sample Preparation

Compact Ge films having a thickness of 260 nm were deposited on molybdenum (Mo) substrates via PECVD. The substrates (Sigma-Aldrich, Mo foil, 3×3 cm, thickness 0.025 mm, $\geq 99.9\%$ trace metals basis) were rinsed in dichloromethane (CARLO ERBA Reagents, RPE grade), acetone (CARLO ERBA Reagents, purity $\geq 99.5\%$), 2-propanol (Sigma-Aldrich, purity $\geq 99.8\%$) and deionised water (in this order) to remove any impurities. After cleaning, the substrates were outgassed inside the antechamber of the PECVD system for 20 min at a temperature of 200°C and a pressure of 2×10^{-6} mbar. The plasma inside the reactor was ignited using 35 sccm of H_2 as the gas carrier and 15 sccm of GeH_4 as the precursor. The deposition occurred at a pressure of 1×10^{-3} mbar and a temperature above 400°C , resulting in a growth rate of 1.26 nm s^{-1} .

Ion implantation on the Ge films was carried out by Ion Beam Services (IBS) S.A.S., France. The samples were irradiated with ^{72}Ge ions at a fluence of $2.5 \times 10^{16} \text{ cm}^{-2}$ and an energy of 150 keV at room temperature. The active mass loading of the resulting samples ranged from 0.22 mg to 0.30 mg and did not change after ion implantation.

2.2 | Morphological and Compositional Characterisation

The surface and cross-sectional morphology of the ion-implanted films were investigated using a scanning electron microscope (SEM) equipped with a focused ion beam (FIB) column (FEI Helios NanoLab DualBeam 650). Before sectioning, the samples were covered with a platinum layer to keep the surface morphology unaltered during FIB erosion. Energy-dispersive X-ray spectroscopy (EDX) maps have been obtained using the same instrument.

The chemical composition and surface morphology of the porous films were characterised using confocal Raman spectroscopy and atomic force microscopy (AFM), respectively. Both measurements were carried out using the LabRam HR Evolution Nano system (Horiba – Jobin Yvon, France), which couples a confocal Raman spectrometer with a scanning probe microscope (Horiba – Omegascope SmartSPM-1000). AFM scans were performed in semi-contact mode using an ACCESS-NC-A probe (AppNano, USA) with a tip radius of less than 10 nm. The oscillation amplitude, set to 60 nm, was used as the feedback parameter, and all scans were acquired at a scan rate of 0.5 Hz with 256 pixels per line over a $6 \times 6 \mu\text{m}^2$ area, with a resonance frequency varying, depending on the acquisition, in the 267–273 kHz range. Row scan data were levelled by surface subtraction to correct for possible sample tilts. Confocal Raman spectroscopy was

performed using a 633 nm laser and a 300 lines mm⁻¹ grating. The laser power on the sample was set to a nominal maximum output of 0.2 mW. The confocal microscope was equipped with a 100× objective, with a numerical aperture (NA) of 0.9, yielding a laser spot diameter of ≈860 nm. After spectra acquisition, a baseline correction was always performed to eliminate the instrumental baseline drift, improving the accuracy of peak identification and intensity analysis. Co-localised AFM and Raman measurements were also performed with this setup. In this mode, the laser spot is precisely focused on the AFM tip using a 100×, 0.9 NA objective, allowing both morphological and chemical characterisation to be performed with their respective lateral spatial resolutions on the exact same surface area.

X-ray diffraction (XRD) was carried out on a Malvern PANalytical Empyrean X-ray powder diffractometer equipped with a 1.8 kW CuKα ceramic X-ray tube operating at 45 kV and 40 mA and a PIXcel^{3D} 2 × 2 area detector. The diffraction pattern was collected in ambient conditions, using a parallel-beam (PB) geometry and symmetric reflection mode.

X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα source (15 kV, 20 mA) to confirm the composition of surface layers on the sample. Wide scans were carried out on an analysis area of 300 × 700 μm and with a pass energy of 160 eV. High-resolution analyses were conducted employing the same analysis area and a pass energy of 10 eV. Spectra have been corrected for sample charging by setting the main line of the carbon 1s spectrum (adventitious carbon) to 284.8 eV and were analysed using CasaXPS software (version 2.3.24) [35].

X-ray reflectivity (XRR) measurements were carried out using a 3rd-generation Malvern-PANalytical Empyrean diffractometer. The instrument was equipped with a 1.8 kW Cu Kα X-ray tube operating at 45 kV and 40 mA, iCore and dCore automated PreFIX optical modules, and a motorised Eulerian cradle (χ, φ, x, y, z) to achieve precise sample alignment. Data were collected using a PIXcel3D solid-state hybrid pixel detector operated in 0D acquisition mode. Measurements were performed in air at room temperature using a zero-diffraction silicon substrate. XRR patterns were recorded over a θ range of 0°–4°, with a step size of 0.005°.

Data analysis and model fitting were conducted using the AMASS v1.1 software package (Malvern-PANalytical). The Ge film was modelled as a single, infinitely thick layer. The density and surface roughness of the layer were the free parameters in the fitting routine. The regression analysis was based on Powell's method.

2.3 | Cell Preparation

The electrochemical behaviour of all electrodes was evaluated using CR2032-format lithium-metal coin cells, using lithium disks from MTI corporation as counter electrodes (diameter 15.6 × 0.45 mm thickness). The electrodes were separated by a glass fibre disk (16 mm diameter, Whatman GF/D) soaked with 200 μL of a 1 M solution of lithium hexafluorophosphate in ethylene carbonate:dimethyl carbonate 1:1 v:v (Sigma-Aldrich) with the addition of 10 wt.% fluoroethylene carbonate (Sigma-Aldrich). The assembly procedure was carried out inside a

MBraun glovebox filled with argon gas (H₂O < 0.1 ppm, O₂ < 0.1 ppm).

2.4 | Electrochemical Characterisation

The electrochemical tests were conducted using a Biologic BCS-805 potentiostat controlled through the BT-Lab software (v1.30). The electrochemical response of the electrodes was characterised through cyclic voltammetry, while their rate capability and stability were characterised by galvanostatic cycling. Cyclic voltammetry was performed at a scan rate of 0.1 mV s⁻¹ in the 0.01–1.5 V voltage range. Moreover, for the characterisation described in section S3 of the Supporting Information, additional cyclic voltammetry scans were performed at 0.05, 0.075, 0.1, 0.15, 0.2 and 0.5 mV s⁻¹. The rate capability test consisted of sets of ten galvanostatic cycles at the following currents (current for a 1C rate equals 1624 mAh g⁻¹ [3]): C/10, C/8, C/4, C/2, 1C, 2C, 4C, 8C, 10C, 20C, 40C and 60C. To evaluate the ability of the cell to recover its capacity after high-rate cycling, 80 cycles at C/10 were performed after cycling at 60C. Moreover, the long-term stability of the electrodes was tested through galvanostatic cycling at a rate of C/4 after three formation cycles at C/10. Both the rate capability and galvanostatic cycling tests were performed employing an upper cutoff voltage of 1.5 V and a lower cutoff voltage of 0.01 V. The stability of bulk, as-deposited electrodes with a thickness of 300 nm was evaluated by galvanostatic cycling at C/4 and 10C within the same voltage window as in the above. Differential capacity analysis (DCA) was performed by calculating the derivative of the transferred charge as a function of cell potential through OriginPro version 2022 from OriginLab Corporation, Northampton, MA, USA. As a preliminary step, a uniform linearly spaced interpolated curve containing 100 data points is calculated using the 'Interpolate/Extrapolate' function. Then, the derivative of this curve is calculated with the 'Differentiate' function. This procedure allows for the obtainment of a noise-free profile.

2.5 | Post-Cycling Analysis

The electrodes for post-cycling analysis were retrieved (in the delithiated state) from the cells that underwent galvanostatic cycling, including the one tested at the constant rate of C/4 and the one that underwent rate capability testing. The disassembly procedure was carried out inside an argon-filled glove box with an MTI MSK-110 crimper equipped with a disassembling die. The electrodes were rinsed with dimethyl carbonate (Sigma-Aldrich, anhydrous, ≥99%) and dried overnight in a vacuum. The analysis was performed using SEM-FIB and XRD to understand how the morphology and crystal structure of the electrodes change in response to cycling (setup in Section 2.2).

3 | Results and Discussion

3.1 | Morphological and Compositional Characterisation

The effect of ion implantation on the PECVD-deposited Ge film was assessed through a complete morphological and compositional characterisation. As shown in Figure 2, ion implantation

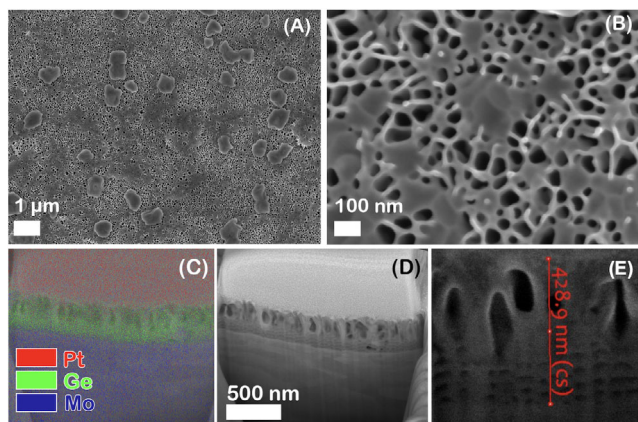


FIGURE 2 | (A) Low-magnification and (B) high-magnification electron micrographs of an ion-implanted Ge film. Cross-sectional (C) EDX map and (D,E) cross-sectional electron micrographs of the same sample with a tilt angle of 52°.

causes the formation of a dense population of nanovoids at the surface of Ge (Figure 2A): their distribution appears non-uniform, with the presence of particle-like agglomerates. These cavities, having diameters ranging from 80 to 100 nm and a honeycomb-like 2D distribution, form a structure resembling a sponge, as shown in Figure 2B. The darkest regions display large and irregular features scattered over the surface.

Mass measurements confirm that no material is removed from the films during ion implantation, implying that the formation of cavities or voids happens through swelling and leads to an increase in thickness [23].

In the EDX map presented in Figure 2C, the nanostructured Ge film is represented in green, between the substrate (Mo, in blue) and a protective layer (platinum, in red), which was deposited to prevent any damage to the nanostructure during sectioning: the SEM micrograph of the same zone can be seen in Figure 2D. In both this figure and in Figure 2E (a higher magnification micrograph of the same sample), nanostructures are only visible in the uppermost part of the film, suggesting that ion implantation could not affect the bottom layer, which appears compact, with no sign of delamination from the substrate. The thickness of the film after implantation was measured from the micrograph in Figure 2E through the control software of the SEM-FIB instrument, considering the 52° tilt angle. From this measurement, the final thickness appears to be ~429 nm, which is 65% more than the original film. Assuming purely out-of-plane expansion, this thickness increase corresponds to an estimated porosity of 39%, indicating that cavities form through swelling [36]. The porosity of the film was more accurately estimated with XRR measurements, as described in the Supporting Information, section S1. The resulting porosity of 39.3% confirms that the assumption of purely out-of-plane expansion is correct.

The short-range atomic ordering of the porous Ge film was characterised through Raman spectroscopy. To do this, four distinct porous regions and four distinct particle-like structures were selected for the analysis using a confocal microscope, ensuring that the selected particles were larger than the area covered by the laser spot. Figure 3 is a comparison between the averaged spectra from particles and porous regions: both exhibit only the characteristic features of amorphous Ge, with a dominant

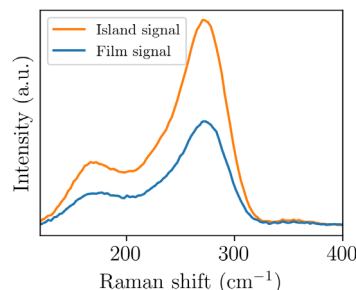


FIGURE 3 | Averaged Raman spectra from four porous film regions and four particle-like structures. The spectra are normalised to the area under the particle-like spectrum.

transverse optical (TO) mode at 276 cm⁻¹, a longitudinal acoustic (LA) mode at 169 cm⁻¹ and its second-order (2LA) around 350 cm⁻¹. The spectral contribution from crystalline Ge, which would appear as an intense, sharp feature around 301 cm⁻¹, is not observed [37, 38]. The difference in photon counts between the two spectra, which were acquired under identical experimental conditions and subjected to the same post-processing, indicates a higher material density in the particle-like structures compared to the porous regions.

The surface topography was analysed in further detail through AFM, leading to the results presented in Figure 4. Within the zone scanned by AFM, the Ge film shows round-shaped agglomerates (Figure 4A–D) with diameters ranging from 1 to 2 μm and a height relative to the porous layer of about 300–400 nm. As is noticeable from Figure 4C, the pores are also detectable by AFM. Moreover, the substrate is evidently not perfectly flat, as it exhibits grooves with depths reaching up to 200 nm.

To correlate the topography with chemical information, AFM/Raman co-localised measurements were performed. The Raman map overlaid to the AFM image in Figure 4E was obtained by integrating all the Raman signal in the range of 220–320 cm⁻¹, corresponding to the main TO mode of amorphous Ge. The colour scale represents the integrated intensity of this spectral region, which is directly correlated with material density. The co-localisation allows for a spatially resolved attribution of the signal, allowing for the distinction between the porous region and the agglomerates, which exhibit the same spectral components. These measurements confirm that both the porous structure and the islands are composed of amorphous Ge [39, 40]. This is as expected since ion implantation into Ge is known to lead to its amorphisation [23].

The chemical makeup of the surface was also investigated in depth through XPS, while the crystal structure was confirmed through XRD. The results are shown in Figure 5A,B, respectively.

The results of the XPS analysis, shown in Figure 5A, indicate that the surface of the film contains germanium, oxygen and carbon, as expected from a film made of pure Ge. The presence of O can be ascribed to the high surface area of the film, which enhances contaminant absorption [41] or due to the formation of native oxides on the film [42]. Furthermore, the latter hypothesis is confirmed by the high-resolution Ge 3d XPS spectrum (inset to Figure 5A) showing signals ascribable both to metallic Ge (peak at ~29.1 eV) and to Ge–O bonds in GeO₂ (peak at ~33.1 eV) [43]. The traces of C are likely due to contamination with adventitious

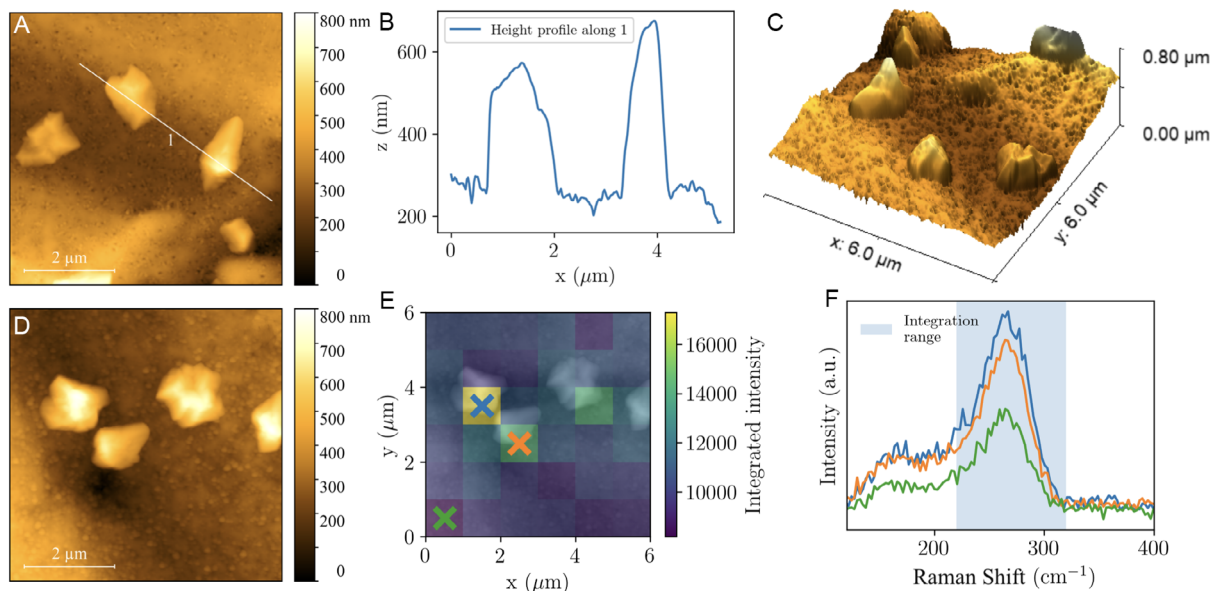


FIGURE 4 | (A) AFM $6 \times 6 \mu\text{m}^2$ map with 256×256 pixels with the corresponding (B) height profile recorded along the white line 1 and (C) 3D representation of the surface. (D) AFM map of the region used for the AFM/Raman co-localised map. (E) AFM/Raman co-localised map and (F) Raman spectra coming from the pixels of the map displayed in 4E. The spectra are normalised to the area under the most intense spectrum (blue curve).

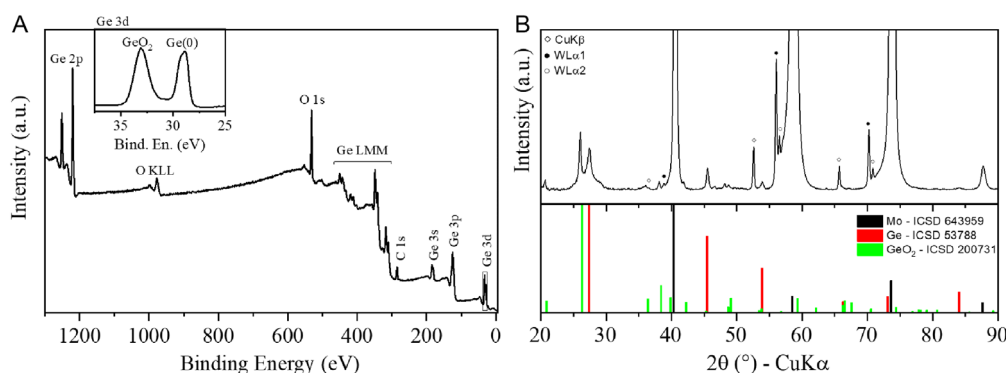


FIGURE 5 | (A) XPS survey scan and (B) X-ray diffractogram of a pristine ion-implanted Ge electrode. The inset to (A) is the high-resolution XPS scan of the energy range characteristic of the photoemission peaks related to Ge 3d levels.

carbon during the exposure to the atmosphere [44]. Regarding the crystal structure of the phases present in the sample, the most intense reflections of the XRD pattern (Figure 5B) belong to the cubic phase of the substrate (Mo, ICSD 643 959). The other reflections arise from the cubic phase of Ge (ICSD 184 252) and the hexagonal phase of GeO_2 (ICSD 59 629), which may be due to the bottom part of the film (i.e., the nonporous section shown in Figure 2E) not being completely amorphous.

3.2 | Electrochemical Characterisation

The electrochemical behaviour of the ion-implanted Ge electrodes was investigated by cyclic voltammetry, obtaining the results reported in Figure 6.

The first cycle (black line in the inset to Figure 6) shows cathodic features right below the open circuit voltage (2.0 V). In particular,

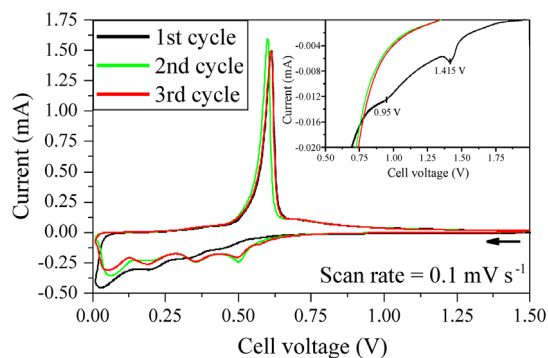


FIGURE 6 | Cyclic voltammetry trace obtained by cycling a lithium metal/ion-implanted Ge cell at a scan rate of 0.1 mV s^{-1} in the 0.01–1.5 V voltage range. The black arrow indicates the starting direction of the CV. The inset is a magnified view of the voltammogram showcasing the peaks related to the formation of the SEI during the first cycle.

the peaks at about 1.4 and 0.9 V, which are absent from the following cycles, can be attributed to the reduction of FEC and the organic solvents during the formation of the SEI [45, 46]. Moreover, the cathodic branch shows several broad peaks below 0.6 V, which can be ascribed to the formation of progressively lithium-rich Li-Ge phases [47, 48]. In particular, the four main cathodic peaks at 0.5, 0.35, 0.19, and 0.06 V are typical of the multistage lithiation process of Ge [32, 33, 48–55]. The anodic branch, on the other hand, always shows a sharp peak at 0.6 V, which is typical of the delithiation reaction of crystalline $\text{Li}_{15}\text{Ge}_4$ to form Ge [52].

The stability of the material to repeated lithiation and delithiation was proven by long-term galvanostatic cycling. In particular, the Ge electrode was first pretreated for SEI formation by cycling the cell at C/10 thrice. Then, the cell was cycled at C/4 for hundreds of cycles. The results of this test are shown in Figure 7. The comparative behaviour of the bulk, as-deposited film, is shown in Figure S2 of the Supporting Information.

The cell exhibited a stable voltage profile (Figure 7A) and a capacity of 1360 mAh g^{-1} for at least 400 cycles (Figure 7B) at a rate of C/4, demonstrating the stability of ion-implanted Ge electrodes during extended cycling. Moreover, the rate capability of the ion-implanted Ge electrodes was characterised through galvanostatic cycling at progressively higher currents, as detailed in Section 2.4. The results of this test are presented in Figure 8.

At low rates, specifically from C/10 to 1C, the voltage profiles (Figure 8A) exhibit no significant polarisation, and the cell delivers a stable capacity of 1415 mAh g^{-1} . This value is slightly above the theoretical one if $\text{Li}_{15}\text{Ge}_4$ is considered to be the end product of the reaction, as it usually is at room temperature [47]. However, this result matches with those of other groups that experimentally observed the formation of an over-lithiated phase $\text{Li}_{15+\delta}\text{Ge}_4$ [47, 52, 53]. The excess capacity we observed is about 31 mAh g^{-1} , corresponding to the formation of a phase with $\delta \sim 0.3$ (~ 0.08 Li excess per Ge atom). When the rate is increased above 1C, polarisation starts to become noticeable, and the capacity progressively drops down to 1390, 1345, 1225 and 1195 mAh g^{-1} at 2C, 4C, 8C and 10C, respectively. To determine whether the behaviour of the system is capacitor-like or battery-like, we conducted the analysis reported in section S3 of the Supporting Information, which demonstrated battery-like behaviour.

Between 2C and 10C, there is a noticeable difference between the first and the last cycle at each rate, with a gradual and partial recovery of the lost capacity. This phenomenon was elucidated through DCA [56], a technique allowing for the detection of the electrochemical processes happening at different cell voltages and their evolution over cycling. We employed this technique to analyse the electrochemical behaviour during the second and last galvanostatic cycles at two selected rates: C/10 and C/2. These rates were selected specifically because one of them did not show the phenomenon of capacity recovery (C/10, Figure 8C), while the other one did (2C, Figure 8D). At C/10, the differential capacity profile (DCP) shows that, during the lithiation of Ge, four main electrochemical processes (showing as four peaks) are at play. During delithiation, on the other hand, there is only one primary electrochemical process happening at 0.5 V: the delithiation of crystalline $\text{Li}_{15}\text{Ge}_4$. These processes are analogous to those observed by cyclic voltammetry and reported in Figure 6. Notably, the DCP of the second and last cycles at C/10 are almost identical, with minor differences arising from the fact that, during the second cycle at C/10, the electrode is still to reach its steady-state electrochemical behaviour. The similarity of the DCPs means that, at C/10, the nature of the electrochemical processes does not change over cycling. When cycling the cell at 2C, however, the DCPs change drastically: in particular, during delithiation, two peaks appear instead of one. The appearance of a peak at about 0.37 V has been convincingly described by Miao et al. [52] as the result of incomplete crystallisation of $\text{Li}_{15}\text{Ge}_4$ at the end of the lithiation process, which has also been reported to happen at high rates by Lim et al. [51]. The intensity of this peak significantly decreases from the second to the last cycle at 2C, while the intensity of the peak at 0.5 V simultaneously increases. This shift in the relative intensities of the two delithiation peaks indicates that, over cycling, the structure of the Ge electrode rearranges in a way that facilitates the crystallisation of $\text{Li}_{15}\text{Ge}_4$, meaning that the kinetics of the electrode improve. At higher rates (from 20C onwards), the rearrangement of the electrode becomes progressively less pronounced, and the capacity starts dropping more noticeably. The reduced degree of rearrangement is probably due to the low extent of reaction at such high rates, which is ascribed to a significantly smaller amount of lithium entering the electrode compared to lower C-rates. Even though the cell cannot keep up with such rates, the electrode still exhibits noteworthy capacities of 830, 490 and 280 mAh g^{-1} at

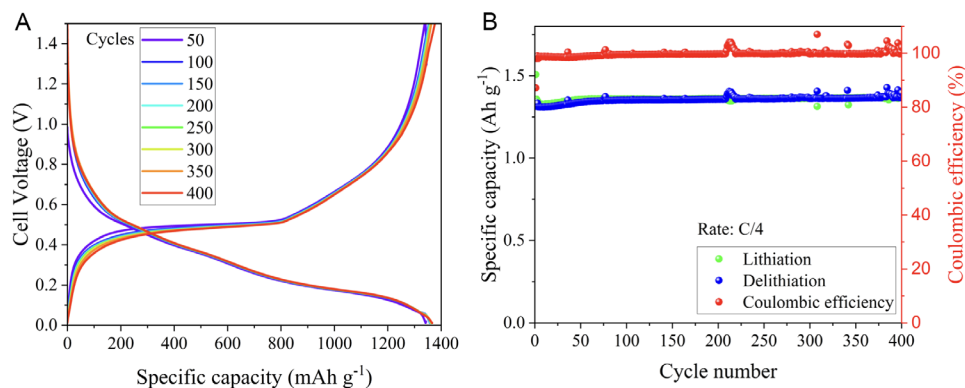


FIGURE 7 | (A) Cell voltage profiles and (B) specific capacity vs cycle number measured during long-term galvanostatic cycling at C/4 of a lithium metal/ion-implanted Ge cell.

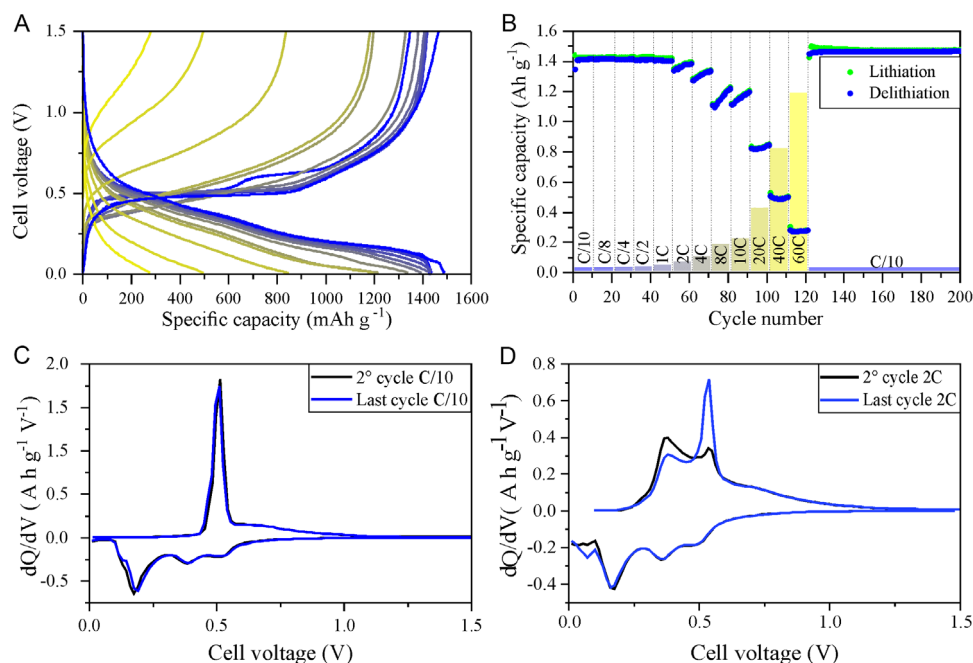


FIGURE 8 | (A) Cell voltage profiles and (B) specific capacity vs cycle number measured during the rate capability tests on a lithium metal/ion-implanted Ge cell. (C,D) Differential capacity vs cell voltage profiles obtained from the data of the second and last cycles at (C) C/10 and (D) 2C.

20C, 40C and 60C, respectively. The electrode also fully recovered and maintained a capacity slightly above the initial one when brought back to C/10, demonstrating its high resilience to the stress imposed by high-rate cycling.

It should be noted that the results reported in this section are in accordance with previous literature reporting the crystallisation of the Li₁₅Ge₄ phase becoming more favoured during extended cycling [52]. However, there is also convincing evidence that, in some cases, the opposite can happen, as reported by Ricci [57], who observed a gradual decrease in the crystalline fraction of Li₁₅Ge₄ during extended cycling. Even though it is well-known that Ge-based electrodes behave very differently depending on the production technique, understanding the reason for such differences is not trivial, and it will require ad-hoc advanced characterisation.

3.3 | Post-Cycling Analysis

To gain a better comprehension of the phenomena happening to the electrodes during the electrochemical characterisation detailed in section 2.4, the crystal structure and morphology of the Ge electrodes were investigated after retrieval from the cells. The results of the analysis carried out on the electrode that underwent galvanostatic cycling at C/4 are shown in Figure 9.

From the diffractogram of the electrode employed for the stability test, shown in Figure 9A, Ge appears to become completely amorphous after prolonged cycling, as the reflections arising from the cubic phase of Ge and the hexagonal phase of GeO₂ are missing. The reflection peaks present in the diffractogram have been attributed to the cubic phase of the substrate (Mo, ICSD:643 959) and to the tetragonal phase of lithium hydroxide (LiOH, ICSD:27543), which is a component of the SEI [58]. From the micrograph of the cross-section of the electrode (Figure 9B)

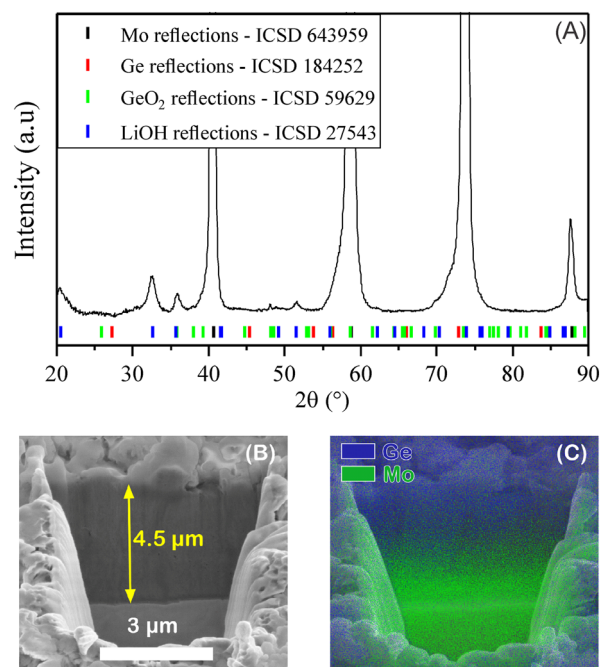


FIGURE 9 | (A) X-ray diffractogram, (B) cross-sectional electron micrograph and (C) EDX map of the Ge electrode retrieved from the cell that underwent extended galvanostatic cycling at C/4.

and the related EDX map (Figure 9C), it can be noticed that the Ge layer increased its thickness from the initial 350 nm to 4.5 μm, which is a more than 1200% increase. Nevertheless, the film still shows uniform adhesion to the substrate, which imparts the electrode with excellent cycling stability (see Figure 7B).

A similar analysis was carried out on the electrode that underwent the rate capability test reported in Figure 8B, obtaining the results reported in Figure 10.

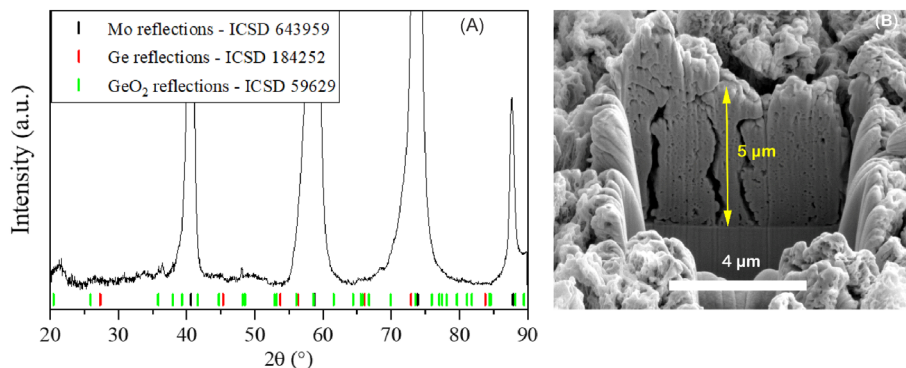


FIGURE 10 | (A) X-ray diffractogram and (B) cross-sectional electron micrograph of the Ge electrode retrieved from the cell that underwent the rate capability test.

The results for this electrode are analogous to those described in Figure 9, with the absence of the reflection peaks of the active material from the diffractogram (Figure 10A) revealing the complete amorphisation of the active layer. The only reflection peaks belong to the cubic phase of the substrate (Mo, ICSD:643959). Similarly to the sample in Figure 10, the micrograph of the cross-section reported in Figure 10B shows the occurrence of a huge expansion of the active material. In this case, however, the structure is porous rather than compact (compare Figure 9B to Figure 10B). This structural change can explain the capacity recovery observed at high rates in the previous section and demonstrates that Ge electrodes produced by combining PECVD and ion-implantation can offer superior high-power performance.

4 | Conclusions

In this study, we have demonstrated the successful production of nanostructured and Ge-based electrodes by combining ion implantation with PECVD. Such well-established and highly reliable semiconductor processing techniques enable a straightforward fabrication process without material removal. The resulting electrode exhibits the remarkable ability to dynamically rearrange its structure to endure high C-rates, making it highly suited for high-power energy storage applications. Beyond high-power scenarios, a semiconductor-compatible battery manufacturing process is also appealing in the context of integrable microbatteries, where low-temperature, layer-by-layer manufacturing is a key requirement. The interest in this field is highlighted by a recent publication on all-solid-state microbatteries equipped with a sputtered silicon thin-film electrode, explicitly targeting low-temperature fabrication and on-chip integration [59]. Integrating Ge-based electrodes into practical devices holds significant promise, particularly in the aerospace sector, which enormously benefits from the weight and volume reduction brought on by using a high-capacity active material. To bring this vision closer to reality, future research should focus on optimising the production method of such electrodes, considering both the deposition and ion implantation processes. Simultaneously, fundamental studies are needed to elucidate the mechanism leading to structural rearrangement. A deeper understanding of this phenomenon would allow for the intentional design of electrode structures that achieve peak

performance from the outset, eliminating the reliance on in-situ structural evolution. By addressing these challenges, future work could pave the way for the efficient integration of nanostructured Ge-based electrodes into next-generation energy storage systems tailored for demanding applications, bridging the gap between fundamental research and industrial-scale manufacturing.

Acknowledgements

This work was supported and financed by the Italian Space Agency (ASI) in the frame of the ANGELS (ANodi in Germanio nanoporoso per batterie al Litio per applicazioni aeroSpaziali) project (grant number ASI_n_2018-1-U.0).

Open access publishing facilitated by Istituto Italiano di Tecnologia, as part of the Wiley-CRUI-CARE agreement.

References

1. G. G. Eshetu, H. Zhang, X. Judez, et al., "Production of High-Energy Li-Ion Batteries Comprising Silicon-Containing Anodes and Insertion-Type Cathodes," *Nature Communications* 12 (2021): 1–14, <https://doi.org/10.1038/s41467-021-25334-8>.
2. S. Liang, Y. J. Cheng, J. Zhu, Y. Xia, and P. Müller-Buschbaum, "A Chronicle Review of Nonsilicon (Sn, Sb, Ge)-Based Lithium/Sodium-Ion Battery Alloying Anodes," *Small Methods* 4 (2020): 2000218, <https://doi.org/10.1002/smt.202000218>.
3. X. Liu, X. Y. Wu, B. Chang, and K. X. Wang, "Recent Progress on Germanium-Based Anodes for Lithium-Ion Batteries: Efficient Lithiation Strategies and Mechanisms," *Energy Storage Materials* 30 (2020): 146–169, <https://doi.org/10.1016/j.ensm.2020.05.010>.
4. S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. P. Zaccaria, and C. Capiglia, "Review on Recent Progress of Nanostructured Anode Materials for Li-Ion Batteries," *Journal of Power Sources* 257 (2014): 421–443, <https://doi.org/10.1016/j.jpowsour.2013.11.103>.
5. J. Graetz, C. C. Ahn, R. Yazami, and B. Fultz, "Nanocrystalline and Thin Film Germanium Electrodes with High Lithium Capacity and High Rate Capabilities," *Journal of the Electrochemical Society* 151 (2004): A698–702, <https://doi.org/10.1149/1.1697412>.
6. C. K. Chan, X. F. Zhang, and Y. Cui, "High Capacity Li Ion Battery Anodes Using Ge Nanowires," *Nano Letters* 8 (2008): 307–309, <https://doi.org/10.1021/nl0727157>.
7. Y. D. Ko, J. G. Kang, G. H. Lee, et al., "Sn-Induced Low-Temperature Growth of Ge Nanowire Electrodes with a Large Lithium Storage

- Capacity," *Nanoscale* 3 (2011): 3371–3375, <https://doi.org/10.1039/c1nr10471c>.
8. X. H. Liu, S. Huang, S. T. Picraux, J. Li, T. Zhu, and J. Y. Huang, "Reversible Nanopore Formation in Ge Nanowires during Lithiation–Delithiation Cycling: An In Situ Transmission Electron Microscopy Study," *Nano Letters* 11 (2011): 3991–3997, <https://doi.org/10.1021/nl2024118>.
9. T. Kennedy, E. Mullane, H. Geaney, M. Osiak, C. O'Dwyer, and K. M. Ryan, "High-Performance Germanium Nanowire-Based Lithium-Ion Battery Anodes Extending over 1000 Cycles through In Situ Formation of a Continuous Porous Network," *Nano Letters* 14 (2014): 716–723, <https://doi.org/10.1021/nl403979s>.
10. L. C. Yang, Q. S. Gao, L. Li, Y. Tang, and Y. P. Wu, "Mesoporous Germanium as Anode Material of High Capacity and Good Cycling Prepared by a Mechanochemical Reaction," *Electrochemistry Communications* 12 (2010): 418–421, <https://doi.org/10.1016/j.elecom.2010.01.008>.
11. M. H. Park, K. Kim, J. Kim, and J. Cho, "Flexible Dimensional Control of High-Capacity Li-Ion-Battery Anodes: From 0D Hollow to 3D Porous Germanium Nanoparticle Assemblies," *Advanced Materials* 22 (2010): 415–418, <https://doi.org/10.1002/adma.200901846>.
12. S. Liu, J. Feng, X. Bian, Y. Qian, J. Liu, and H. Xu, "Nanoporous Germanium as High-Capacity Lithium-Ion Battery Anode," *Nano Energy* 13 (2015): 651–657, <https://doi.org/10.1016/j.nanoen.2015.03.039>.
13. Z. Sun, Q. Yin, H. Chen, et al., "Building Better Solid-State Batteries with Silicon-Based Anodes," *Interdisciplinary Materials* 2 (2023): 635–663, <https://doi.org/10.1002/idm2.12111>.
14. Z. Hu, S. Zhang, C. Zhang, and G. Cui, "High Performance Germanium-Based Anode Materials," *Coordination Chemistry Reviews* 326 (2016): 34–85, <https://doi.org/10.1016/j.ccr.2016.08.002>.
15. X. Xiao, X. Li, S. Zheng, J. Shao, H. Xue, and H. Pang, "Nanostructured Germanium Anode Materials for Advanced Rechargeable Batteries," *Advanced Materials Interfaces* 4 (2017): 1600798, <https://doi.org/10.1002/admi.201600798>.
16. Z. Ju, X. Zhang, J. Wu, et al., "Tortuosity Engineering for Improved Charge Storage Kinetics in High-Areal-Capacity Battery Electrodes," *Nano Letters* 22 (2022): 6700–6708, <https://doi.org/10.1021/acs.nanolett.2c02100>.
17. A. Y. Kozmenkova, S. D. Farafonova, E. A. Saverina, et al., "Electrochemical Etching of Germanium in Ionic Liquids without the Use of Toxic and Corrosive Reagents," *Chemnanomat : Chemistry of Nanomaterials for Energy, Biology and More* 7 (2021): 1355–1360, <https://doi.org/10.1002/cnma.202100338>.
18. S. Tutashkonko, S. Alekseev, and T. Nychporuk, "Nanoscale Morphology Tuning of Mesoporous Ge: Electrochemical Mechanisms," *Electrochimica Acta* 180 (2015): 545–554, <https://doi.org/10.1016/j.electacta.2015.08.112>.
19. V. Diolaiti, A. Andreoli, S. Chauque, et al., "Comparison of Porous Germanium Thin Films on SS and Mo as Anode for High-Performance LIBs," *IEEE Transactions on Nanotechnology* 22 (2023): 552–557, <https://doi.org/10.1109/TNANO.2023.3311757>.
20. N. M. Lyadov, T. P. Gavrilova, S. M. Khantimerov, et al., "Formation of Pores in Thin Germanium Films under Implantation by Ge⁺ Ions," *Technical Physics Letters* 46 (2020): 707–709.
21. N. G. Rudawski, B. R. Yates, M. R. Holzworth, K. S. Jones, R. G. Elliman, and A. A. Volinsky, "Ion Beam-Mixed Ge Electrodes for High Capacity Li Rechargeable Batteries," *Journal of Power Sources* 223 (2013): 336–340, <https://doi.org/10.1016/j.jpowsour.2012.09.056>.
22. N. G. Rudawski, B. L. Darby, B. R. Yates, K. S. Jones, R. G. Elliman, and A. A. Volinsky, "Nanostructured Ion Beam-Modified Ge Films for High Capacity Li Ion Battery Anodes," *Applied Physics Letters* 100 (2012): 083111, <https://doi.org/10.1063/1.3689781>.
23. L. Romano, G. Impellizzeri, M. V. Tomasello, F. Giannazzo, C. Spinella, and M. G. Grimaldi, "Nanostructuring in Ge by Self-Ion Implantation," *Journal of Applied Physics* 107 (2010): 084314, <https://doi.org/10.1063/1.3372757>.
24. R. A. Susantyoko, X. Wang, L. Sun, K. L. Pey, E. Fitzgerald, and Q. Zhang, "Germanium Coated Vertically-Aligned Multiwall Carbon Nanotubes as Lithium-Ion Battery Anodes," *Carbon* 77 (2014): 551–559, <https://doi.org/10.1016/j.carbon.2014.05.060>.
25. W. Li, Z. Yang, J. Cheng, X. Zhong, L. Gu, and Y. Yu, "Germanium Nanoparticles Encapsulated in Flexible Carbon Nanofibers as Self-Supported Electrodes for High Performance Lithium-Ion Batteries," *Nanoscale* 6 (2014): 4532–4537, <https://doi.org/10.1039/C4NR00140K>.
26. N. G. Rudawski and K. S. Jones, "Nanostructured Germanium Prepared via Ion Beam Modification," *Journal of Materials Research* 28 (2013): 1633–1645, <https://doi.org/10.1557/jmr.2013.24>.
27. I. H. Wilson, "The Effects of Self-Ion Bombardment (30–500 keV) on the Surface Topography of Single-Crystal Germanium," *Journal of Applied Physics* 53 (1982): 1698–1705, <https://doi.org/10.1063/1.331636>.
28. A. M. Rogov, V. I. Nuzhdin, V. F. Valeev, and A. L. Stepanov, "Formation of Porous Germanium Layers with Various Surface Morphology in Dependence on Mass of Implanted Ions," *Composite Communications* 19 (2020): 6–10, <https://doi.org/10.1016/j.coco.2020.01.002>.
29. V. V. Bazarov, V. A. Shustov, N. M. Lyadov, et al., "Studying Near-Surface Layers of Germanium Implanted with Cobalt Ions," *Technical Physics Letters* 45 (2019): 1047–1049, <https://doi.org/10.1134/S1063785019100183>.
30. Y. Hamedani, P. Macha, T. J. Bunning, R. R. Naik, and M. C. Vasudev, *Advances and Applications in Optical, Solar Cells and Solid State Devices* (London: IntechOpen, 2016).
31. S. Chen, C. Niu, H. Lee, et al., "Critical Parameters for Evaluating Coin Cells and Pouch Cells of Rechargeable Li-Metal Batteries," *Joule* 3 (2019): 1094–1105, <https://doi.org/10.1016/j.joule.2019.02.004>.
32. S. Fugattini, U. Gulzar, A. Andreoli, et al., "Binder-Free Nanostructured Germanium Anode for High Resilience Lithium-Ion Battery," *Electrochimica Acta* 411 (2022): 139832, <https://doi.org/10.1016/j.electacta.2022.139832>.
33. V. Diolaiti, A. Andreoli, P. Bernardoni, et al., "Nano structured Germanium Anode for Lithium-Ion Batteries for Aerospace Technologies," in *Proceedings of the IEEE Conference on Nanotechnology*, (2022), 56–59.
34. J. F. Ziegler, "Stopping of Energetic Light Ions in Elemental Matter," *Journal of Applied Physics* 85 (1999): 1249–1272, <https://doi.org/10.1063/1.369844>.
35. N. Fairley, V. Fernandez, M. Richard-Plouet, et al., "Systematic and Collaborative Approach to Problem Solving Using X-Ray Photoelectron Spectroscopy," *Applied Surface Science Advances* 5 (2021): 100112, <https://doi.org/10.1016/j.apsadv.2021.100112>.
36. B. Stritzker, R. G. Elliman, and J. Zou, Self-Ion-Induced Swelling of Germanium, *Nuclear Instruments and Methods in Physics Research Section B*, 2001, pp. 193–196, 175–177, [https://doi.org/10.1016/S0168-583X\(00\)00597-8](https://doi.org/10.1016/S0168-583X(00)00597-8).
37. H. S. Alkhalidi, F. Kremer, T. Bierschenk, et al., "Porosity as a Function of Stoichiometry and Implantation Temperature in Ge/Si_{1-x}Ge_x Alloys," *Journal of Applied Physics* 119 (2016): 094303, <https://doi.org/10.1063/1.4942995>.
38. J. D. Owen, J. R. Troutman, T. A. Harriman, et al., "The Mechanics of Milling of Germanium for IR Applications," *CIRP Annals* 65 (2016): 109–112, <https://doi.org/10.1016/j.cirp.2016.04.076>.
39. I. D. Desnica-Franković, K. Furić, U. V. Desnica, M. C. Ridgway, and C. J. Glover, Structural Modifications in Amorphous Ge Produced by Ion Implantation, *Nuclear Instruments and Methods in Physics Research*

- Section B, 2001, pp. 192–195, 178, [https://doi.org/10.1016/S0168-583X\(00\)00489-4](https://doi.org/10.1016/S0168-583X(00)00489-4).
40. Z. Hao, S. A. Kochubei, A. A. Popov, and V. A. Volodin, “On Raman Scattering Cross Section Ratio of Amorphous to Nanocrystalline Germanium,” *Solid State Communications* 313 (2020): 113897, <https://doi.org/10.1016/j.ssc.2020.113897>.
41. O. W. Holland, B. R. Appleton, and J. Narayan, “Ion Implantation Damage and Annealing in Germanium,” *Journal of Applied Physics* 54 (1983): 2295–2301, <https://doi.org/10.1063/1.332385>.
42. D. Schmeisser, R. D. Schnell, A. Bogen, et al., “Surface Oxidation States of Germanium,” *Surface Science* 172 (1986): 455–465, [https://doi.org/10.1016/0039-6028\(86\)90767-3](https://doi.org/10.1016/0039-6028(86)90767-3).
43. National Institute of Standards and Technology, *NIST X-Ray Photoelectron Spectroscopy Database*, version 5.0,” Accessed July 15 (2023): 2025, <https://doi.org/10.18434/T4T88K>
44. L. H. Grey, H. Y. Nie, and M. C. Biesinger, “Defining the Nature of Adventitious Carbon and Improving Its Merit as a Charge Correction Reference for XPS,” *Applied Surface Science* 653 (2024): 159319, <https://doi.org/10.1016/j.apsusc.2024.159319>.
45. C. Xu, F. Lindgren, B. Philippe, et al., “Improved Performance of the Silicon Anode for Li-Ion Batteries: Understanding the Surface Modification Mechanism of Fluoroethylene Carbonate as an Effective Electrolyte Additive,” *Chemistry of Materials* 27 (2015): 2591–2599, <https://doi.org/10.1021/acs.chemmater.5b00339>.
46. D. C. Bock, A. C. Marschlok, K. J. Takeuchi, and E. S. Takeuchi, “Deliberate Modification of the Solid Electrolyte Interphase (SEI) during Lithiation of Magnetite, Fe_3O_4 : Impact on Electrochemistry,” *Chemical Communications* 53 (2017): 13145–13148, <https://doi.org/10.1039/C7CC07142F>.
47. H. Jung, P. K. Allan, Y. Y. Hu, et al., “Elucidation of the Local and Long-Range Structural Changes That Occur in Germanium Anodes in Lithium-Ion Batteries,” *Chemistry of Materials* 27 (2015): 1031–1041, <https://doi.org/10.1021/cm504312x>.
48. S. Goriparti, U. Gulzar, E. Miele, et al., “Facile Synthesis of Ge-MWCNT Nanocomposite Electrodes for High Capacity Lithium Ion Batteries,” *Journal of Materials Chemistry A* 5 (2017): 19721–19728, <https://doi.org/10.1039/C7TA04971D>.
49. X. H. Liu, Y. Liu, A. Kushima, et al., “In Situ TEM Experiments of Electrochemical Lithiation and Delithiation of Individual Nanostructures,” *Advanced Energy Materials* 2 (2012): 722–741, <https://doi.org/10.1002/aenm.201200024>.
50. L. Y. Lim, N. Liu, Y. Cui, and M. F. Toney, “Understanding Phase Transformation in Crystalline Ge Anodes for Li-Ion Batteries,” *Chemistry of Materials* 26 (2014): 3739–3746, <https://doi.org/10.1021/cm501233k>.
51. L. Y. Lim, S. Fan, H. H. Hng, and M. F. Toney, “Storage Capacity and Cycling Stability in Ge Anodes: Relationship of Anode Structure and Cycling Rate,” *Advanced Energy Materials* 5 (2015): 1500599, <https://doi.org/10.1002/aenm.201500599>.
52. J. Miao, B. Wang, and C. V. Thompson, “Kinetic Study of Lithiation-Induced Phase Transitions in Amorphous Germanium Thin Films,” *Journal of the Electrochemical Society* 167 (2020): 090557, <https://doi.org/10.1149/1945-7111/ab9eec>.
53. A. Al-Obeidi, D. Kramer, C. V. Thompson, and R. Mönig, “Mechanical Stresses and Morphology Evolution in Germanium Thin Film Electrodes during Lithiation and Delithiation,” *Journal of Power Sources* 297 (2015): 472–480, <https://doi.org/10.1016/j.jpowsour.2015.06.155>.
54. C. Zhong, J. Z. Wang, X. W. Gao, D. Wexler, and H. K. Liu, “In Situ One-Step Synthesis of a 3D Nanostructured Germanium–Graphene Composite and Its Application in Lithium-Ion Batteries,” *Journal of Materials Chemistry A* 1 (2013): 10798–10804, <https://doi.org/10.1039/c3ta11796k>.
55. D. H. Lee, D. H. Kim, H. Jung, and C. M. Park, “Li Reaction Pathways in Ge and High-Performance Ge Nanocomposite Anodes for Li-Ion Batteries,” *Chemical Engineering Journal* 454 (2023): 140329, <https://doi.org/10.1016/j.cej.2022.140329>.
56. A. J. Smith and J. R. Dahn, “Delta Differential Capacity Analysis,” *Journal of the Electrochemical Society* 159 (2012): A290, <https://doi.org/10.1149/2.076203jes>.
57. Marco Ricci, University of Genoa, (2024). *Development of Stable and High-Power Germanium/Lithium Iron Phosphate Lithium-Ion Cells*, Doctoral dissertation, https://doi.org/10.15167/ricci-marco_phd2024-03-26
58. A. Wang, S. Kadam, H. Li, S. Shi, and Y. Qi, “Review on Modelling of the Anode Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries,” *Npj Computational Materials* 4 (2018): 64, <https://doi.org/10.1038/s41524-018-0064-0>.
59. B. Ke, C. Zhang, S. Cheng, et al., “Tape-Casting Electrode Architecture Permits Low-Temperature Manufacturing of All-Solid-State Thin-Film Microbatteries,” *Interdisciplinary Materials* 3 (2024): 621–631, <https://doi.org/10.1002/idm2.12174>.

Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Supporting Fig. S1:** Reflected X-ray intensity vs. angle for BGe (red trace) and PGe (blue trace) films. **Supporting Fig. S2:** Specific capacity plot vs. number of cycles of a BGe electrode in a lithium-metal cell cycled at C/4 and 10C rates. **Supporting Fig. S3:** Current vs cell voltage recorded during voltammetric scans at different rates. **Supporting Fig. S4:** Log-log plot of the anodic peak current (i_{peak}) versus scan rate (v) for the main redox feature located in the 0.5–0.75 V region. The solid line represents the linear fit to the equation $\log i_{\text{peak}} = \log a + b \log v$; the fitting parameters are reported in the inset.