Electronic Supplementary Material (ESI) for Energy Advances.


# Electronic Supplementary Information

# Lithiation/Delithiation of Silicon Heavily Doped with Boron Synthesized Using the Czochralski Process

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**Table S1.** Summary of undoped Si (11N) and B- and P-doped Si synthesized by a Czochralski method: dopant species, concentration, electrical conductivity, lattice constant, initial charge−discharge capacities, and Coulomb efficiency.

| Sample | Dopant | Concentration / ppm (at.%) [a] | Atomic density / atoms $cm^{-3}$ | Electrical conductivity / mΩ cm [b] | Lattice constant / Å [c] | 1st capacities / mA h $g^{-1}$ | 1st C.E. (%) |
|---|---|---|---|---|---|---|---|
| 1) | - (11N) | Undoped | $5.0 \times 10^{22}$ | $10^{8}$ | 5.431 | 3364 / 3915 | 86 |
| 2) | P | 2000 (0.20) | $1.0 \times 10^{20}$ | 0.9 | 5.431 | 3389 / 3828 | 89 |
| 3) | B | 300 (0.03) | $1.5 \times 10^{19}$ | 6.5 | 5.429 | 3402 / 3943 | 86 |
| 4) | B | 1600 (0.16) | $8.0 \times 10^{19}$ | 1.6 | 5.428 | 3359 / 3920 | 86 |
| 5) | B | 4700 (0.47) | $2.4 \times 10^{20}$ | 0.6 | 5.425 | 3284 / 3786 | 87 |
| 6) | B | 12400 (1.24) | $6.2 \times 10^{20}$ | 0.3 | 5.415 | 2979 / 3622 | 82 |

a) ICP by an alkali fusion method.
b) Four-terminal type impedance measurement.
c) Estimated value from the dopant concentration (ref.1).
Ref.1) G. Masetti, M. Severi, S. Solmi, *IEEE Trans. Electron Devices*, **30** (1983) 764−769.

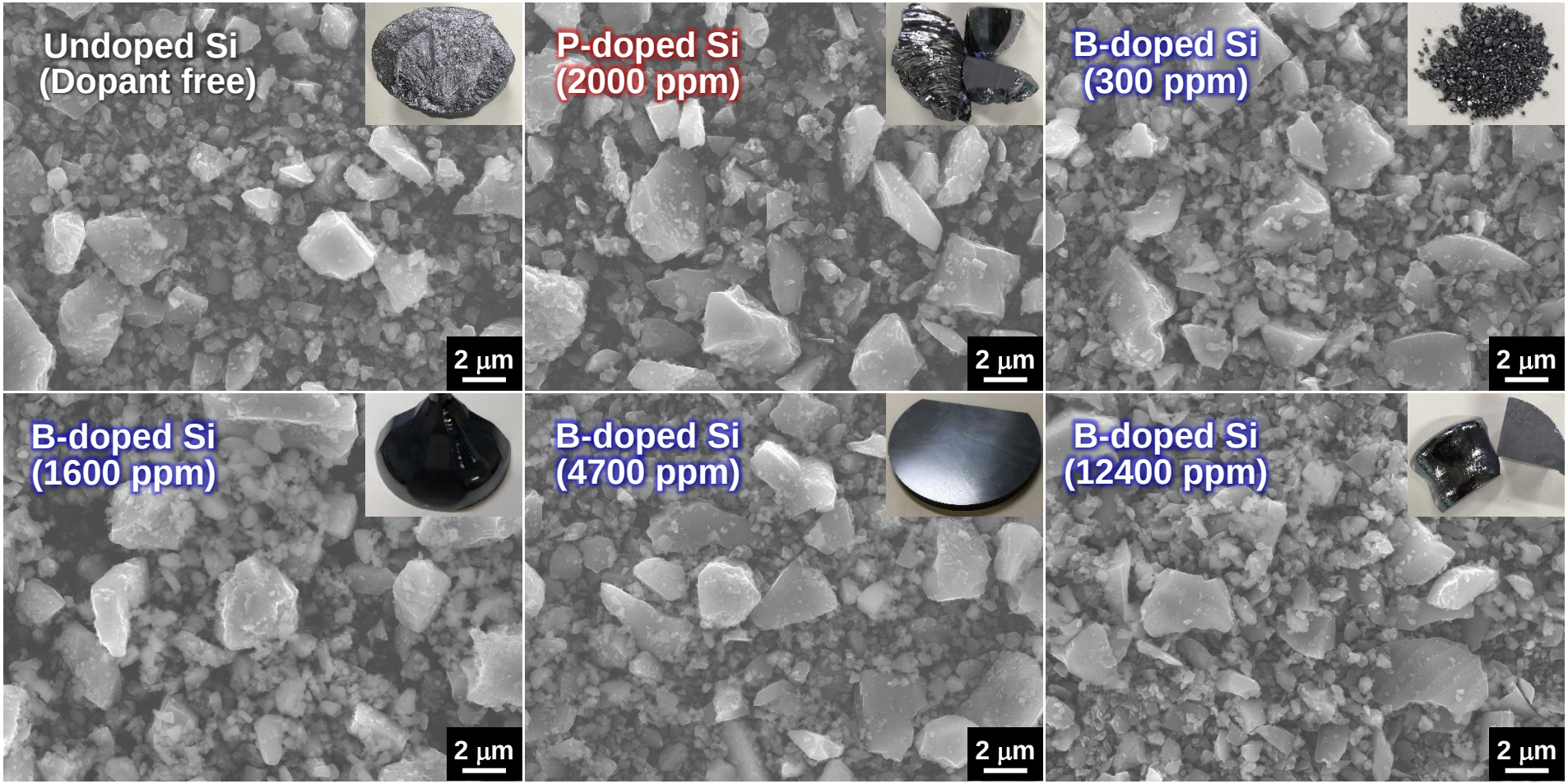


**Figure S1.** SEM images of 11N-Si (dopant free), P-doped Si (2000 ppm), B-doped Si (600, 1600, 4700, 12400 ppm) powders crushed by mechanical milling. Insets: Si ingots prepared by the Czochralski method (300 ppm-B doped Si: crushed granules). the 300 ppm-B doped Si was prepared form a diluted melt of the Si with highly concentrated B and polycrystalline Si.

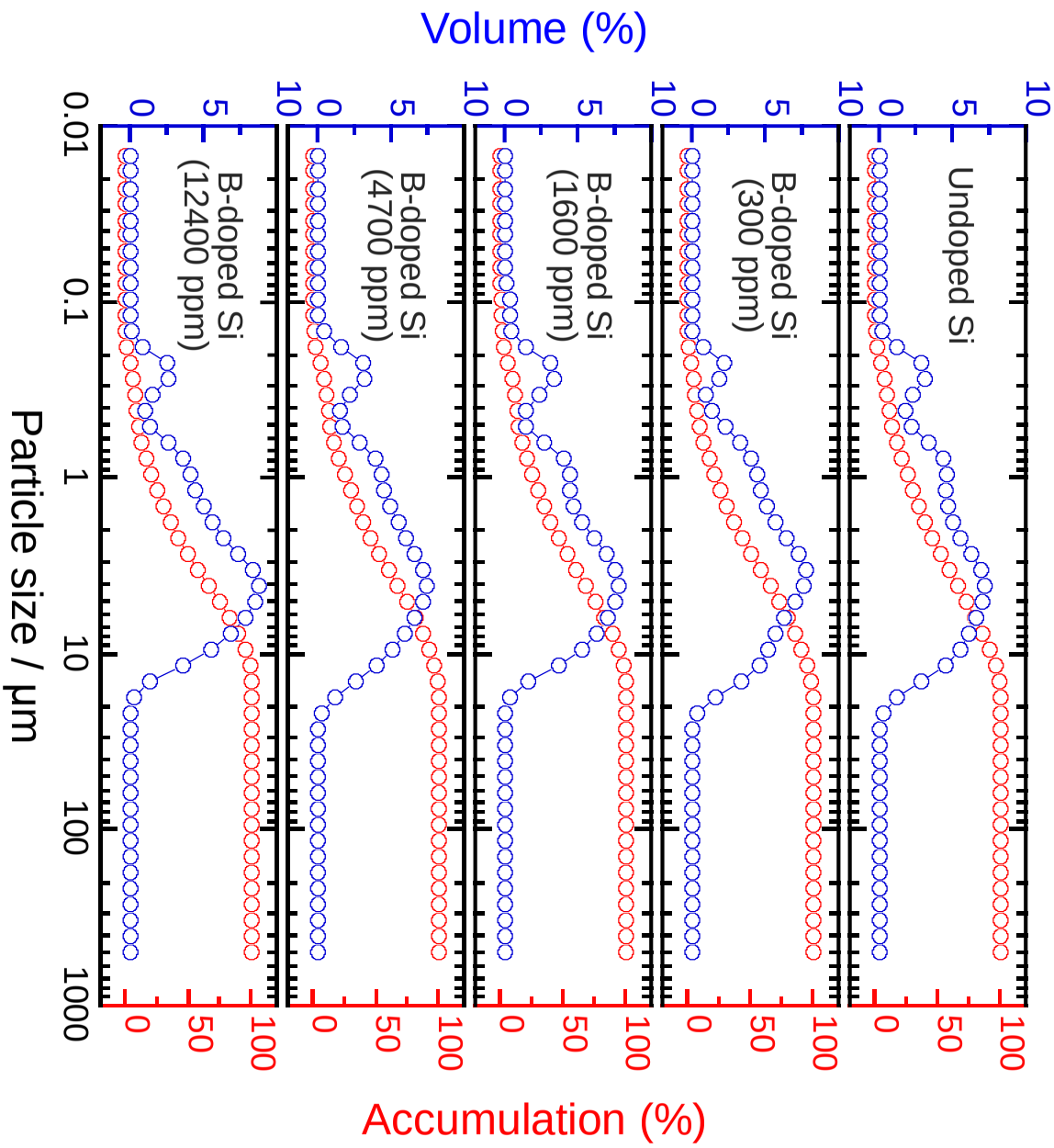


**Figure S2.** Particle size distributions of 11N-Si (dopant free) and B-doped Si (600, 1600, 4700, 12400 ppm) powders used in the preparation of mixture electrodes in this work. Ingots were fractured to granule size in a mortar prior to mechanical milling (MM). The respective MM times were set to keep the particle size distributions about the same.

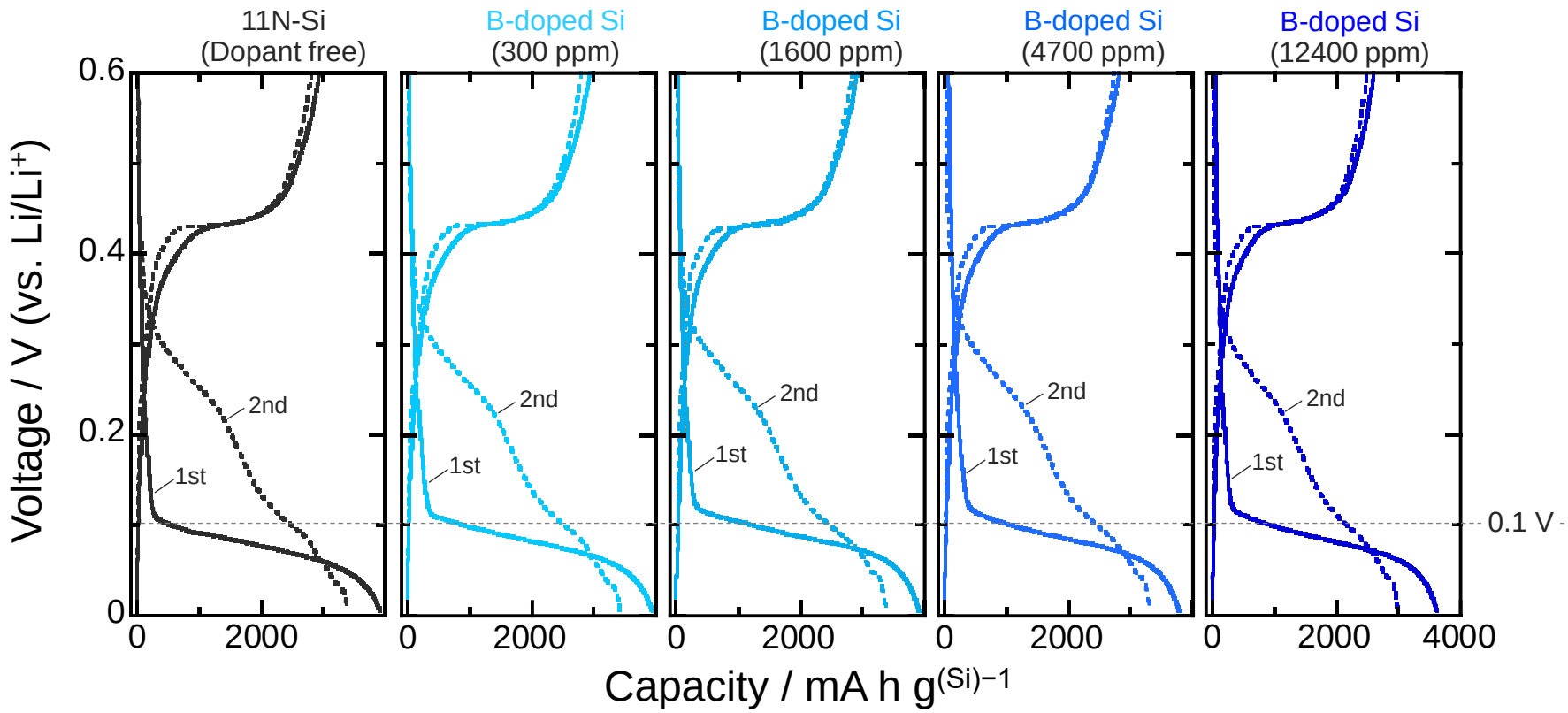


**Figure S3.** Enlarged view of galvanostatic charge−discharge curves (Figure 2a) of undoped (dopant free) and B-doped Si (600, 1600, 4700, and 12400 ppm) electrodes in 1 M $LiPF_6$/EC:DEC (50:50 vol.%) at a current density of 358 mA $g^{-1}$ (0.1*C*). The onset voltages of lithiation for the B-doped Si are higher than that of the undoped Si irrespective of B concentrations.

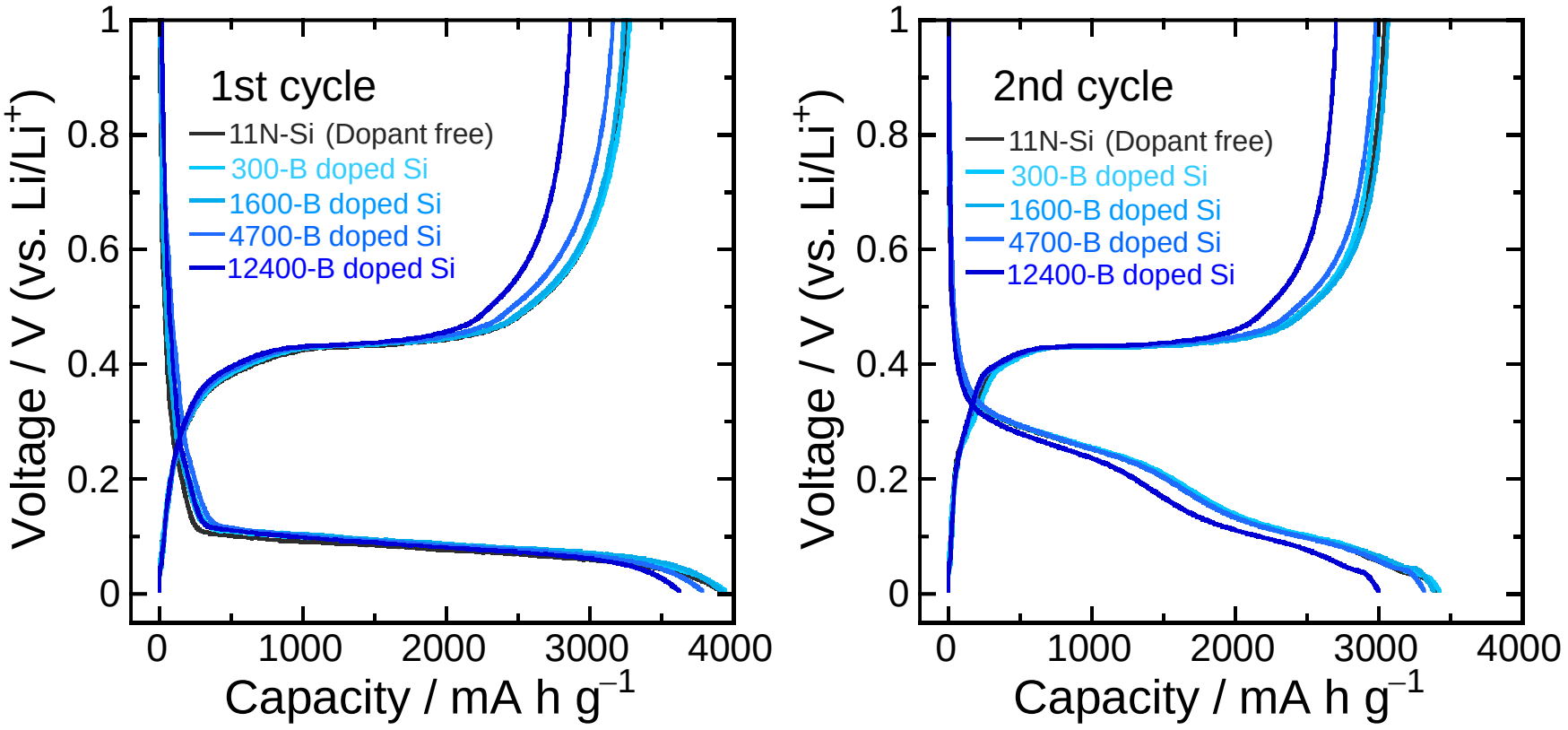


**Figure S4.** Comparison of first and second charge−discharge curves (Figure 2a) of undoped (dopant free) and B-doped Si (600, 1600, 4700, and 12400 ppm) electrodes in 1 M $LiPF_6$/EC:DEC (50:50 vol.%) at a current density of 358 mA $g^{-1}$ (0.1*C*). The onset voltages of lithiation for the B-doped Si are higher than that of the undoped Si irrespective of B concentrations.

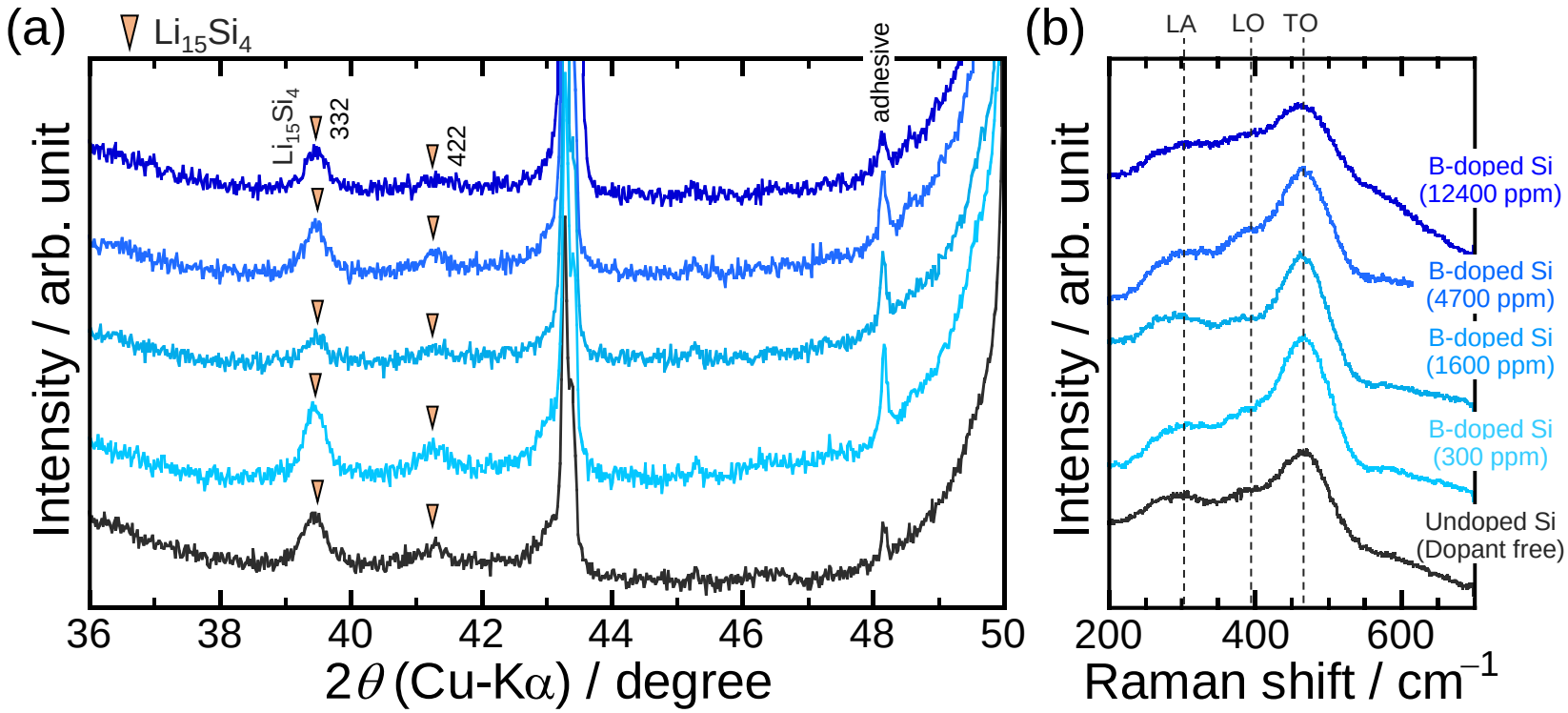


**Figure S5.** (a) XRD patterns of undoped Si and B-doped (300, 1600, 4700, 12400 ppm) Si electrodes at the lithiation voltage of 0.005 V (vs. $Li/Li^+$). The electrodes were charged and discharged at a current density of 358 mA $g^{-1}$ (0.1*C*). (b) Raman spectra of undoped Si and B-doped Si electrodes after the first delithiation (upper cut-off voltage: 2.0 V). Crystalline Si undergoes amorphization after the first lithiation/delithiation process to transform into amorphous Si, which was observed from the Raman spectra. After the first cycle, the vibrations of Si–B ($^{11}B$, $^{10}B$) bonds were not detected.

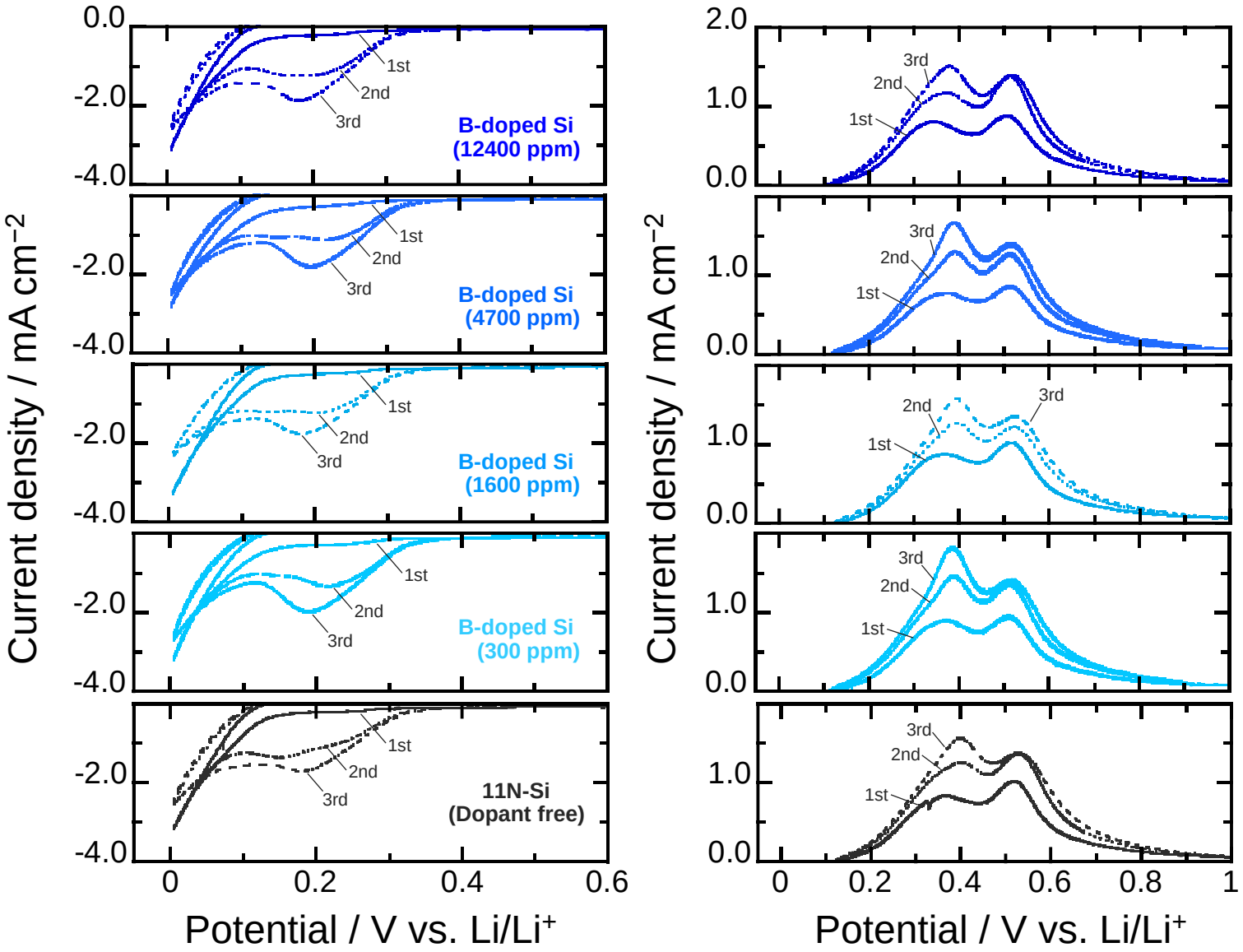


**Figure S6.** Cyclic voltammograms of undoped and B-doped Si (600, 1600, 4700, and 12400 ppm) electrodes in 1 M $LiPF_6$/EC:DEC (50:50 vol.%) at a sweep rate of 0.1 mV $s^{-1}$. Left: cathodic scan, Right: anodic scan.

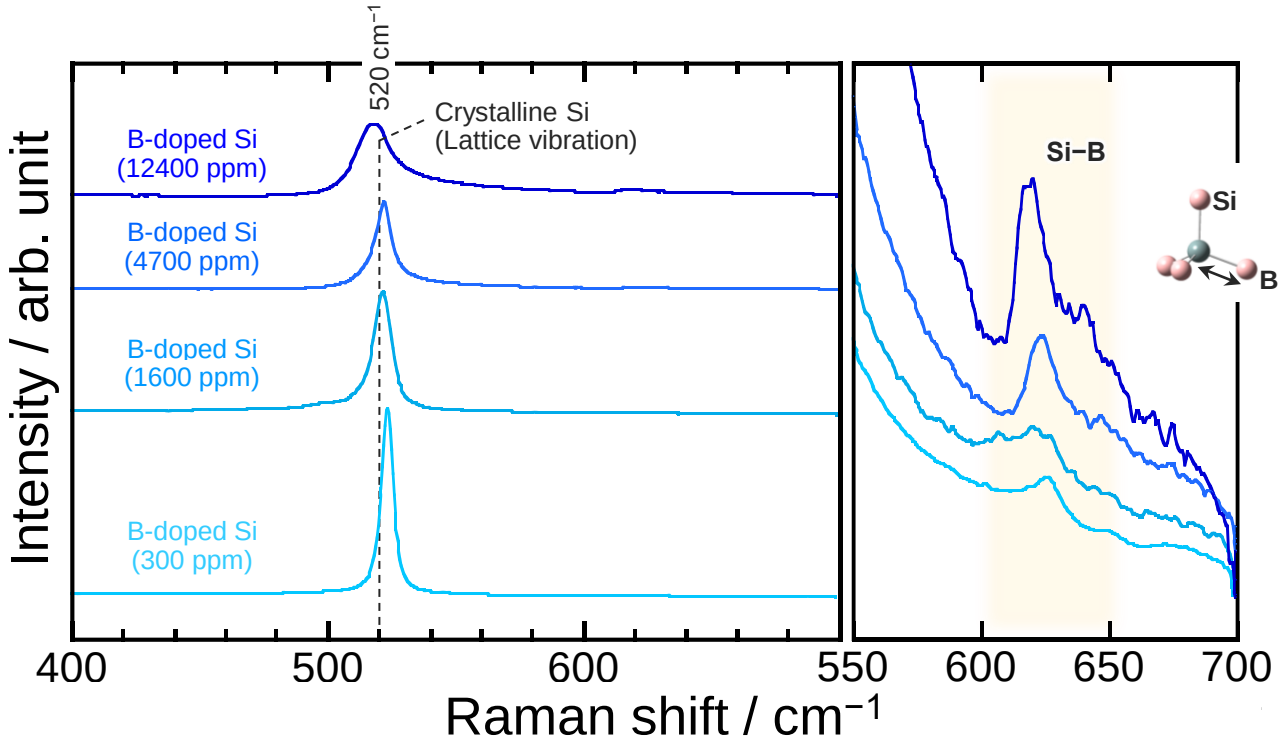


**Figure S7.** Raman spectra of undoped Si and B-doped Si electrodes crystallized by the laser irradiation (wavelength: 532 nm) for 30 min. The undoped Si and B-doped Si electrodes were charged and discharged for one cycle at a current density of 358 mA $g^{-1}$ (0.1*C*), which resulted in the amorphization of the Si and the B-doped Si. The vibrations of Si–$^{11}$B and Si–$^{10}$B bonds were again detected. Therefore, even in the case of the pulverization and fracture of the active material due to the huge volume change in Si during lithiation/delithiation, the conductive network of the entire electrode structure is expected to be maintained.

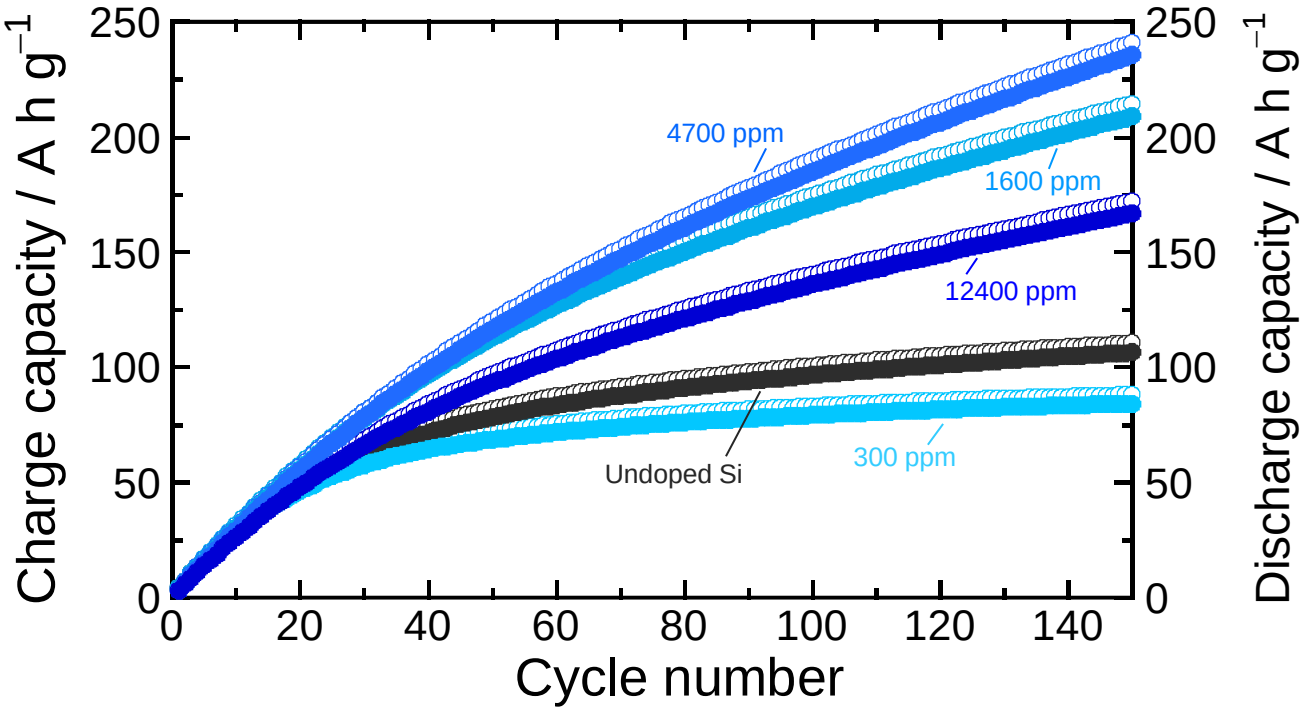


**Figure S8.** Dependence of integrated lithiation/delithiation capacity of B-doped Si electrodes under the galvanostatic condition with a current density of 358 mA g$^{-1}$ (0.1*C*). The lithiation/delithiation capacities of at the 4700 ppm-B doped Si at the initial cycles are slightly smaller than those of the 1600 ppm-B doped Si, meaning that the degree of volume change is also relatively lower. The lower volume change appears to result in the better cycling performance, but rather, the 4700 ppm-B doped Si actually has larger integrated capacities after the 100 cycles.