# Improving Nano/Micro Porous Silicon Electrode Properties by Ultra-thin Atomic Layer Deposited (ALD) high-k oxide passivation for High Energy Density Li-Ion Battery Application

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Silicon (Si) has been investigated as a lithium-ion battery anode due to its high theoretical capacity (4200 mAh/cm$^2$) over carbon electrodes (372 mAh/cm$^2$). Although Si provides high energy capacity due to high order $Li_xSi$ alloy ratios, it suffers from high semi-irreversible volumetric expansion upon lithiation. The 200-300% volumetric increase causes structural cracking and electrode detachment resulting in early electrode failure [1]. Structured electrodes such as porous Si and nanowires have shown to provide some strain relaxation but still suffer from electrode dislocation. To overcome this issue, ultra-thin oxide passivation on Si has been introduced [2]. The purpose of such a barrier layer is to allow ionic diffusion while maintaining the mechanical stability of the electrode against radial expansion. In this study, the effect of Atomic Layer Deposited (ALD) high-k oxide passivation on the early cycling property of porous Si (PS) electrode was investigated.

PS was fabricated by electrochemical etching of crystalline n-Si (100) in HF/Ethanol/$H_2O_2$ solution. The fabricated PS structure after etching is shown in Fig. 1. Three different barrier layers ($Al_2O_3$, $TiO_2$, and $HfO_2$) were then deposited in thermal ALD reactor at 200°C on PS structure. The thickness of each ALD oxide layer is set to be 2nm based on the deposition rate. Half-cell batteries were constructed with Li metal anode and PS cathodes. Cyclic voltammetry (CV) was performed to compare early cycling characteristics of each dielectric.

CV was performed for 10 cycles at 1mV s$^{-1}$ starting from a discharge cycle and the potential range is 25mV – 2V vs. Li/Li+ reference electrode. The first discharge cycle is significantly different than subsequent cycles for each sample (Fig. 2). This difference is attributed to the solid electrolyte interface (SEI) formation [3]. Bare PS exhibits a large reduction current during the first cycle as shown in Fig. 2 (a). It is believed that the anodic peak current decrease in subsequent cycles may reflect continuing volumetric changes in the Si layer, where some porous layer detachment may be occurring. Fig. 2 also shows a cathodic peak formation in all samples at E≈540mV vs. Li/Li+ indicating the lithiation process [3]. After 10 cycles, the bare PS sample demonstrates continuous change in the anodic branch and increasing lithiation peaks in the cathodic branch. Samples with ALD dielectric passivation seem to stabilize within the 10 cycles and demonstrate growing lithiation peaks without further anodic current decay. The electrode stabilization process is different for different oxide passivation materials compared to the bare sample when comparing the anodic peak current ratio from cycles 2 and 10 as seen in Fig. 3. Peak cathodic current is related to the lithiation process (taken at the 10$^{th}$ cycle), where increasing values correspond to higher Li insertion. As expected, the addition of oxide barrier layers seems to reduce Li insertion into the PS layer and prevents lower order alloy ratios as indicated by the lower cathodic peak current after 10 cycles and lack of $Li_{12}Si_7$ peak at E=330mV vs. Li/Li+. Among three ALD dielectrics ($Al_2O_3$, $TiO_2$, and $HfO_2$) $HfO_2$ shows the least discharge current fade and comparable cathodic peak current to bare PS in early cycle evaluations. These CV characteristics may relate to the physical strength of $HfO_2$ [4] encasing the amorphized Si, allowing for higher Li loading content.

This work evaluates the effect of ultra-thin ALD oxide barrier layer on the early cycling characteristics of porous Si electrode for LIB application. It was found that porous Si with $HfO_2$ dielectric passivation retains about 90% of the initial capacity after 10 cycles whereas porous Si with $Al_2O_3$ or $TiO_2$ passivation shows 80% retention. It was also found that the ALD oxide passivation reduces lower cathodic peak current as compared to the porous Si without oxide passivation. HfO2 demonstrates the highest cathodic peak among the ALD oxides, corresponding to the highest concentration of $Li_7Si_3$.

This work was supported by ASSIST ERC Program of the National Science Foundation under Award Number EEC-1160483. The authors thank to Dr. W. Qu and R. Rajagopalan at Penn State University for the battery assembly.

## References

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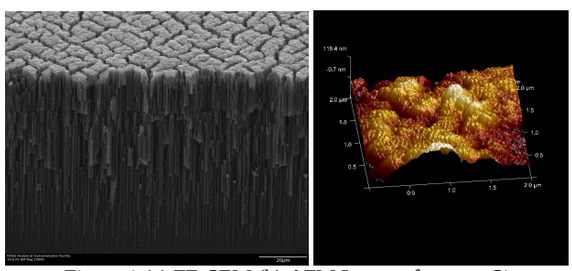

Figure 1 (a) FE-SEM (b) AFM Image of porous Si

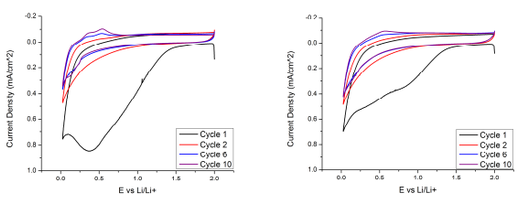


Figure 2. CV of porous silicon: (a) Bare (b) $HfO_2$

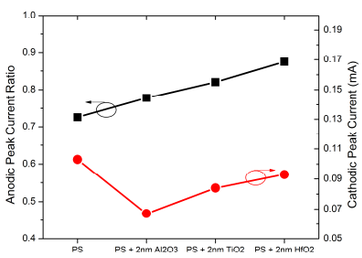


Figure 3. Comparison of peak CV current vs. barrier layer