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High Power and High Capacity 3D-Structured TiO2 Electrodes for Lithium-Ion Microbatteries

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An on-chip compatible method to fabricate high energy density TiO2 thin film electrodes on 3D-structured silicon substrates was demonstrated. 3D-structured electrodes are fabricated by combining reactive ion etching (RIE) with low pressure chemical vapor deposition (LPCVD), enabling accurate control of the aspect ratio of substrates and the subsequent deposition of TiO2 thin film electrodes onto these structured substrates. The prepared 3D-TiO2 electrodes exhibit a current-dependent increase in storage capacity of a factor up to 16 as compared to conventional planar electrodes. In addition, these 3D electrodes also reveal excellent power and cycling performance. This work demonstrates that LPCVD is capable of depositing homogenous film electrodes on highly structured substrates and the prepared 3D-electrodes also shows significant improve in storage capacity and power density.

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Nowadays, many electronic products are becoming smart and connected. Thousands of wireless sensors are integrated into networks collect useful data that make our lives safer and more convenient. As sensors, wireless communication devices, personal health monitoring systems and autonomous microelectromechanical systems (MEMS) become more widespread and individual sensor nodes become more compact,1,5 there is an increasing demand for integrated power systems and autonomous microelectromechanical systems (MEMS) design useful data that make our lives safer and more convenient. As sensors, wireless communication devices, personal health monitoring systems and autonomous microelectromechanical systems (MEMS) become more widespread and individual sensor nodes become more compact.1,5 There is an increasing demand for integrated power systems and autonomous microelectromechanical systems (MEMS) and MEMS-type devices, the available area is limited. Traditional performance indicators of batteries, namely gravimetric, volumetric energy and power densities are therefore less relevant. Instead, the real issue is how much energy a device can deliver per footprint area, measured in terms of mAh·cm−2, J·cm−2 or μW·mm−2, etc.16 TiO2 has been considered as a promising electrode for Li-ion batteries as it is safe, non-toxic, readily available and long cycle stability. However, the poor conductivity and slow diffusion rate of Li+ in TiO2 has restricted the rate capability and storage capacity of TiO2.15,16 A potential solution to overcome this limitation is simply by decreasing the thickness of the film. However, nano-sizing the film thickness typically leads to severe capacity reduction. Employing 3D-TiO2 thin film electrodes is, however, a promising method to solve this dilemma.17–19

Several reports have demonstrated that 3D-TiO2 electrodes reveal a higher footprint areal storage capacity and power performance.17,18,20–22 However, since these methods are not directly based on Si substrate technology, integrating these 3D batteries onto chips or micro-sensors would be very challenging. Besides, in some work, the applied deposition method is atomic layer deposition (ALD),17,18,20 The ALD processes are complicated and the growth rate is slow, limiting large scale production. Reactive ion etching (RIE) and low pressure chemical vapor deposition (LPCVD) are two commonly used techniques in the semiconductor industry. The RIE method is very convenient in creating periodically micro-structured 3D substrates with high aspect ratios and LPCVD is capable of producing high quality, high-performance thin films.23–25 Here, we report a flexible and on-chip 3D microbatteries by combining the techniques of RIE with LPCVD. Two kinds of 3D-structured substrates with varying...
3D-structured TiO₂ electrodes are investigated. One kind of 3D substrate is Si trenches; the other is Si pillars. Trench substrates are convenient to prepare samples for cross-section view to check the uniformity of deposited films. Due to more open space, Si pillar substrates are more convenient for mass production and easy to be coated with other films. In this study, for the first time, homogeneous 3D-TiO₂ thin film electrodes are deposited by LPCVD in 3D Si trenches and on Si pillar substrates. The energy and power densities and cycle life of these electrodes deposited by LPCVD in 3D Si trenches and on Si pillar substrates. The energy and power densities and cycle life of these 3D-structured TiO₂ electrodes are investigated.

Experimental

Thin film deposition.—(100) oriented silicon wafers were used as starting material. In order to increase the effective surface area of the Si substrates, etching of trenches with aspect ratios of 1 and 3 and Si pillars with length of 50 μm was conducted using photolithography and RIE, of which the parameters were published before.26 The MOCVD setup used for TiO₂ deposition has been described in detail in a previous publication.23 In short, a cold wall MOCVD reactor (Aixtron 200 RF) was used, in which the substrate was positioned on a radio frequency heated susceptor. The precursor was titanium(IV) isopropoxide (TTIP), acquired from SAFC-Hitech (United Kingdom). TTIP was delivered in a stainless steel bubbler. This bubbler was thermostated at 25 °C, and the pressure was controlled at 300 mbar. The flow rate of argon through the bubbler to evaporate TTIP was fixed at 100 sccm, while the total flow through the reactor was 1550 sccm. The deposition temperature was varied from 350 to 550 °C. Argon was used as carrier gas. The pressure of the reactor was 5 mbar during the deposition processes.

TiO₂ films for thickness and surface morphology analyses were deposited onto square silicon substrates with a width of 3 cm. The planar TiO₂ electrodes prepared for electrochemical measurements were deposited on similar substrates covered with an adhesive barrier layer of TiN (30 nm) and a layer of platinum (70 nm) as current collector. To investigate the uniformity of the 3D deposition, TiO₂ films were deposited onto structured silicon substrates, in which trenches with a depth of 30 μm and width of 30 and 10 μm were etched with RIE, as shown in Figs. 2a and 2b, respectively. To investigate the electrochemical performance of 3D-TiO₂ electrodes, the films were deposited on silicon into which a pillar structure was etched.

The pillars were coated with 30 nm TiN by ALD, which was used as current collector. The diameter and height of the Si pillars are 2 μm and 50 μm, respectively, and the distance between pillars is 5 μm. SEM images of these pillar substrates are shown in Figs. 2c and 2d. The surface enlarging factor (A) of the pillar substrate used for the electrochemical investigations is calculated, according to

\[ A = 1 + \pi dh/(d + l)^2 \]

where d and h represent the diameter and length of pillars, respectively. l is the distance between Si pillars.

Sample characterization.—The thickness and morphology of the TiO₂ thin films were analyzed, using a scanning electron microscope (SEM, Philips/FEI XL 40 FEG). Measurements of Raman spectra were performed on an Olympus BX-40 Raman Spectrometer under a backscattering geometry. A 633 nm line of a Helium-Neon laser was taken as the excitation source. The electrochemical measurements were performed in an argon-filled glove box (O₂ and H₂O < 1 ppm). The samples were positioned in Teflon cells and used as working electrodes. Lithium metal foils were utilized as reference and counter electrodes. The cell was filled with 1 M LiClO₄ in propylene carbonate (Soulbrain MI, United States) as electrolyte. This three-electrode setup was connected to a M2300 galvanostat (Maccor, Tulsa, USA) to perform galvanostatic (dis)charging from 0 to 3 V vs. Li/Li⁺ at different current densities: 4, 8, 20, 40 and 80 μA per cm² footprint area. All electrochemical tests were carried out at room temperature (∼22 °C).

Results and Discussion

The SEM images of TiO₂ films deposited at different temperatures are shown in Figs. 3a–3d. It is clear that all films are homogeneous without revealing any cracks or pinholes, which is an apparent advantage of LPCVD to deposit high quality thin films. The simplicity of the deposition process also permits the processing of large wafer batches. It is interesting to note that the thicknesses of films deposited at higher temperatures, 400, 450 and 550 °C, are close to each other, but much thicker than the films deposited at 350 °C, which indicates a significant increase of growth rate from 350 to 400 °C.

The Raman spectra of the deposited films are shown in Fig. 4 as a function of deposition temperature. The Raman spectra of the four films are very similar to each other, showing small peaks at 396 and 639 cm⁻¹ and very sharp and intense peak at 144 cm⁻¹, which match well with the reported Raman bands for anatase.27 It can therefore be concluded that all deposited TiO₂ films have the anatase structure.

Fig. 5 shows the Arrhenius plot of the growth of planar TiO₂ films. It is obvious that the growth of TiO₂ films can be divided into two parts,
Raman spectroscopy of TiO₂ films deposited at various temperatures, indicating that there are two different rate-determining processes in these temperature ranges. At high temperatures the deposition rate is only weakly dependent on the deposition temperature. Increasing the deposition temperature from 450 to 550°C only result in a small increase of growth rate, which indicates that in this temperature range the growth of TiO₂ is a diffusion controlled process.²⁸ In contrast, in the low-temperature region where the slope in Fig. 5 is much steeper, the deposition rate is strongly dependent on the temperature. Here, the activation energy calculated from Fig. 5 is 63.4 kJ/mole, which is relatively high, indicating the deposition of TiO₂ at 350°C is a kinetically controlled process.²⁸ Therefore, it was concluded that the deposition rate was limited by diffusive transport in the high-temperature range, while at lower temperatures the deposition is a kinetically controlled process. Within the kinetically controlled region, the growth rate is relatively slow, implying that the chemical conversion of Ti-precursor during the transportation of precursor gas into trenches is slow. Thus, there will still be sufficient Ti-precursor available for the growth of the TiO₂ film even toward the bottom of the trench. A uniform deposition at different parts of the 3D substrate can therefore be expected under these conditions.

Figs. 6a–6c shows a TiO₂ film deposited on different sections (I, II, III and IV) of a 10 μm wide trench. The applied deposition temperature is 350°C, clearly within the kinetically controlled temperature region. Obviously, the deposited film is very homogeneous from top to bottom. Fig. 6d shows the development of deposited film thickness as a function of distance from the top surface to the bottom on two trench substrates with different widths, 30 and 10 μm. For both trenches, the films deposited on the top part of the substrates are around 287 nm thick and slightly thinner at bottom, indicating a very high step coverage. Consistent with the prediction from the Arrhenius plot, the film deposited at 350°C is very uniform.

To show the advantages of 3D-electrodes in improving both the capacity and power performances, TiO₂ thin film electrodes have been deposited on TiN-covered 3D micro-pillar substrates to investigate the electrochemical performances. Fig. 7a shows the tilt-view of a pillar substrate. Based on geometrical calculations, the surface area enlargement factor is 7.4. Figs. 7b–7d show the film thickness distribution.
of a TiO₂ film deposited at 350°C on the surface of Si pillars. A film with layer thickness of 80 nm is deposited on the top surface. At the bottom of the Si pillars, the film thickness is 75 nm. A step coverage of 94% was achieved.

For LPCVD, the deposited film thickness increases linearly with deposition time. The thickness of TiO₂ electrodes can be easily adjusted by changing the deposition time. In order to achieve a high power performance, thin TiO₂ films (40 nm) were chosen as demonstrator. The voltage curves of a planar and a 3D-structured TiO₂ electrode at different (dis)charging current densities are shown in Figs. 8a and 8b, respectively. For these electrodes, the typical (dis)charging behavior of anatase TiO₂ is shown. Voltage plateaus at ∼1.7 and ∼2.0 V were observed in the charge-discharge curves of both planar and 3D TiO₂ film anodes, which can be attributed to the insertion and extraction of Li⁺ through Li-poor tetrahedral TiO₂ and the Li-rich orthorhombic Li₁₀.₆TiO₂, respectively. Although more Li can be accommodated in Li₁₀.₆TiO₂ to form Li₂TiO₂ by further two-phase intercalation, the reaction is known to have sluggish kinetics. For current density of 80 μA·cm⁻², the storage capacity of the 3D electrode is 6 times higher than that of the planar electrode at the same current density. It is also worthwhile to note that even at the highest current density applied (80 μA·cm⁻²), the capacity of the 3D electrode is still twice as high as the storage capacity of the planar electrode at low current densities, i.e. at 4 μA·cm⁻². Obviously, the power performance per footprint area of TiO₂ is significantly improved by the 3D-structure.

For the 3D-electrodes, the surface area is enlarged by 7.4 times, which means that 7.4 times more TiO₂ has been deposited within the same footprint area compared to planar electrodes. Therefore, for 3D-electrodes, a 1 C-rate equals to 78.2 × 0.04 × 7.4 = 23.1 μA·cm⁻². For current density of 80 μA·cm⁻², the C-rate for 3D-electrodes is 80/23.1 = 3.5 C. Obviously, under the same output power, the actual C-rate of 3D-electrodes is much lower than for planar-electrodes, resulting in a better power performance. This improvement becomes more pronounced at high output powers. As shown in Fig. 8d, the storage capacity improvement of 3D electrodes with respect to planar electrodes is more significant as the current density increases. At 80 μA·cm⁻², the storage capacity of the 3D electrode is 66.2 μAh·cm⁻²·μm⁻¹, which is 16 times higher than that of the planar electrode at the same current density.

As shown in Fig. 8c, at all applied current densities, the 3D electrode shows much higher storage capacities than the planar electrode. For a planar TiO₂ electrode, the storage capacity quickly decreases with increasing (dis)charging current. At 80 μA·cm⁻², the storage capacity has dropped to 4.1 μAh·cm⁻²·μm⁻¹, which is less than 14% of the initial capacity. Contrastingly, the storage capacity of the 3D-TiO₂ electrode measured at 80 μA·cm⁻² is 66.2 μAh·cm⁻²·μm⁻¹, which is 16 times higher than that of the planar electrode at the same current density. The voltage of a planar TiO₂ electrode is 3.89 g·cm⁻¹, which means that 7.4 times more TiO₂ has been deposited within the 3D-structure.

For the 3D-structured TiO₂ film electrode. For a 40 nm planar electrode, 1 C equals to 78.2 × 0.04 = 3.1 μA·cm⁻². So, the (dis)charging current densities of 4 and 80 μA·cm⁻² correspond to a 1.3 and 25.8 C-rate for planar electrodes, respectively. It is noticed that the overpotentials of 3D TiO₂ electrode are smaller than for planar electrodes, especially at high (dis)charging current density, which indicates that 3D TiO₂ electrode have better power performance.
becomes higher, even exceeding the surface area enlargement. This further manifests the advantage of the 3D electrode geometry in improving the power performance, especially at high (dis)charging current densities.

Fig. 9 shows the energy density as a function of power density for the planar and 3D TiO2 electrodes. It is clear that at all output powers, the 3D TiO2 film electrode reveals a higher capacity. Or alternatively, at a given storage capacity, the 3D electrode delivers a much higher power output. Based on the above discussion of electrochemical results, it is clear that by applying the concept of 3D film electrode, the storage capacity and power performance of thin film electrodes can be improved simultaneously.

The cycling performance of 3D and planar TiO2 film electrodes is shown in Fig. 10. The applied current density per footprint area is 4 μA·cm⁻². During the entire cycling test, the 3D TiO2 anode shows much higher storage capacity than the planar electrode. This is mainly attributed to the enlarged surface area, which allows more TiO2 loaded per footprint area. What’s more, up to almost 400 cycles, the 3D electrode doesn’t show any significant capacity decay, demonstrating excellent cycle performance.

Conclusions

A flexible and accurate 3D fabrication route to create 3D microbattery electrodes by combining RIE with LPCVD was demonstrated. It has been found that the LPCVD deposition of TiO2 thin films can be divided into a diffusion-controlled and a kinetically-controlled temperature region. Employing deposition conditions within the kinetically-controlled region, uniform 3D-TiO2 electrodes have been deposited by LPCVD. Compared with planar TiO2 electrodes, the storage capacity of 3D-TiO2 electrodes increased more than 6 times at low current density (4 μA·cm⁻²) and even 16 times at high current densities (80 μA·cm⁻²). This high storage capacity is maintained even after 450 cycles. Besides the significant improvement of the storage capacity, the power performance is also improved. At all output power densities, the 3D electrodes manifest a higher storage capacity than planar electrodes. The present results open new strategy for depositing electrode materials on complicated 3D-substrates by using LPCVD. It also clearly demonstrates the advantages of 3D electrodes for improving both the storage capacity and power performance of thin film batteries.

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