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Fabrication of three dimensional substrates for Li microbatteries on Si.

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Abstract.

Lithographic techniques for patterning planar substrates to achieve microbattery materials compatible three dimensional (3D) Ni substrates for sequential deposition of active battery materials are described. A single spin negative photoresist is used to achieve 100 µm pattern heights. After patterning, Ni is electroplated on the substrates from a low stress Ni sulfamate bath to a maximum of 100 µm. The sidewall angle achieved yields a thinner Ni feature at the surface level than at the base which is a key parameter to facilitate subsequent active battery materials deposition by vacuum deposition techniques. An aspect ratio of 1.5:1 has been achieved and the surface area is increased by comparison with planar electrodes.

Keywords; Microfabrication; 3D; Microbattery; Anode; Silicon; Lithium

1. Introduction

There has been an increasing interest in recent years for lithium ion microbatteries for microelectromechanical systems (MEMs) integrated devices on silicon substrates [1]. These thin film electrodes and electrolyte may be fabricated on patterned substrates and then integrated on chip to match the specific requirements of the systems. Minimising the footprint of such devices while maintaining the capacity and current drain capability is desirable to maximise the integration per substrate. Some research has been published on three dimensional electrodes via lithographic techniques and half cell Li tests [3-5]. Homogeneous deposition of active electrode films on these substrates is a major task. This paper deals with developing the patterning process of a negative photoresist (BPR 100) to achieve structures with sidewall angles that permit active materials deposition by vacuum based line-of-sight techniques. These 3D architecture deposition processes must be compatible with the microbattery fabrication techniques currently in use in the microelectronic industry.

2. Experimental

2.1 Lithographic process and 3-d structuring of Ni.

The lithographic process is illustrated schematically in Fig. 1. A layer of BPR 100 negative photoresist (Rohm and Haas Electronic materials LLC) was spun on 200 nm sputter deposited Cu over a 20 nm Ti adhesion layer on a 100 mm diameter Si wafer then baked at 85 °C for 40 min. The wafer was then UV exposed and post baked at 80 °C for 20 min. A Karl Suss MJB 45S mask aligner was used for UV exposure at 8 mW/sec and

a total dosage of 800 mJ/cm^2. BPR photo-developer was used to develop the processed wafer. Ni was electroplated onto the developed areas from low stress Ni sulphamate bath 5 A/dm^2 at 50 °C at pH of 3.8. Ni was plated to 100 µm at 1 µm/min. The electrolyte pH solution was adjusted by 1M sulphamic acid. The remaining photoresist was finally removed using BPR photoresist stripper at 50 °C for 20 min.

2.2 Evaporation of Indium tin oxide

1 µm thick Indium tin oxide (ITO) was evaporation deposited from Umicore ITO pellets on 3D patterned Ni substrates. The evaporation was carried out in a Leybold LAB600 e-beam evaporator at a base pressure of 2x10^{-6} mbar. The chamber was back filled with O_2 at 6 sccm. The pressure was 1x10^{-4} mbar. The evaporation was Ar^+ assisted with ion energy at 72 eV and ion current at 430 mA. The evaporation rate was 2 Å/sec. The substrates were fixed to a rotating carousel.

2.3 Microstructure analysis.

X-ray diffraction of as-deposited films was performed on a Panalytical/Phillips X'pert MPD equipped with Cu K α radiation source. Stoller slits of 0.2 degrees were used and goniomerter resolution of 0.001 degrees. Scanning electron microscopy (SEM) studies were performed on Hitachi S4000. The deposited films were then electrochemically tested for Li storage.

2.4 Li cycling behaviour of active materials.

The Li cycling behaviour of the deposited ITO films was recorded using a potentiostat (Model CH 660B) in a three electrode cell under inert atmosphere (O_2 and H_2O < 0.1 ppm) in an argon recirculating glove box. In the three-electrode cell, the ITO was the working electrode and Li foil being counter and reference electrodes. The electrolyte was 1M lithium hexafluorophosphate ($LiPF_{6)}$ in a 1:1 volume solution mixture of ethylene carbonate (EC) and di-ethyl carbonate (DEC).

3. Results & Discussion

3.1 3D Ni microstructures.

Figs 2 (a and b) show electroplated Ni arrays on Si wafer substrates with a sidewall angle of 99°. BPR photoresist layers of 100 µm thick were challenging to formulate while maintaining the integrity of the desired sidewall angles. This angle was maintained by annealing at 90 °C after developing the wafer and a maximum sidewall angle of 105° could be achieved in this approach. Ni line feature sizes as small as 60 µm with aspect ratios of 1.5:1 were achieved despite processing these photoresist at elevated temperatures (100 °C). This substrate design is appropriate for sequential multilayer deposition of active battery materials which may be used without any change in process control. (e.g. by sputtering or e-beam evaporation)

3.2 Evaporated ITO

The active material investigated in this work is ITO. Such materials are of interest as potential Li anode materials [6 - 8]. This is also a well established material for planar

deposition and therefore useful for comparison with the 3D deposits of the current work. X-ray diffraction results show (Fig. 3) that the deposited ITO films have oxides of Sn and In and traces of In metal. JCPDS data file 72-1012 matches to SnO (2θ = 29.8°, 62°) show (101) and (211) orientations and the In matches to 01-1042 file (2θ = 33°, 69°) show (002) and (222) respectively. In_2O_3 matches to 06-0416 file (2θ -68°) show hkl indices of (721).

Fig 4 shows SEM images of as-deposited ITO films on 3D Ni microstructures. Homogenous deposition was observed with no post annealing of deposited films required. Cross sectional analysis shows uniform deposition of ITO on the Ni. The non vertical sidewall angle assists the uniform deposition of evaporated material. The available surface area is increased in this way and more active material can be deposited for increased Li storage capacity.

3.3 Lithium cycling of ITO.

The cyclic voltammograms were recorded at 0.5 mV/s between 1.2 V and 0.0 V vs. Li^+/Li. Figs. 5(a) shows lithium cycling behaviour on planar e-beam evaporated ITO film and 5 (b) on 3D substrates respectively. As observed in previous studies [7 - 9] it is expected that the initial reactions are the reaction of Li ions with the oxides of Sn and In. Li alloying/de-alloying with the unoxidised metals then occurs at potentials closer to 0 V vs. Li^+/Li. It appears that the Li starts to react with the oxides over the potential range 1.1V to 0.5V. Below this the Li^+ ions interaction with Sn and In metals and form alloys of up to $Li_{4.33}M$ (M represents Sn or In). The first cycle exhibits a large irreversible

reduction wave resulting from the reaction of Li^+ with the oxides [7 - 9]. After the large first cycle capacity loss the system reaches steady state behaviour in the second cycle. Li storage capacity values of In_2O_3 are considerably smaller [7] than Li storage in SnO_2 and at approximately 200 mAh/g. Li has been reported to intercalate with SnO_2 to ~ 400 mAh/g over repetitive cycling [8]. It is expected that uniformly deposited active material, ITO in our case, on microstructured substrates should increase the active surface area by a factor > 2.0. Li reacts with 1 μm ITO films and intercalates to a maximum current density of 300 $\mu A/cm^2$ on planar substrates as shown in first cycle in Fig. 5 (a) and 600 $\mu A/cm^2$ on 3D Ni in Fig. 5(b). The increase in surface area is observed as an increase in current density during Li intercalation in the ITO films and the values are doubled for 80 μm Ni structured samples. Fig. 6 shows the lithium storage capacity values of the first ten cycles of ITO on planar and 3D Ni (100 and 80 μm) substrates. At cycle 3, the capacity for planar ITO is 24 $\mu Ah/cm^2$, for 100 μm Ni features it is 48 $\mu Ah/cm^2$ and for 80 μm Ni features 64 $\mu Ah/cm^2$. At cycle 8 this has decreased to 18 $\mu Ah/cm^2$ for the planar and 48 $\mu Ah/cm^2$ for 80 μm samples which indicates a similar rate of capacity decrease for the planar and 3D substrates.

4. Conclusion

Thick film spin on negative photoresist (BPR 100) was used to 3D pattern Ni microstructures to increase the battery material capacity per unit footprint. The sidewall angle of the resist was processed to enable Ni microstructures onto which the vacuum deposited active material could be uniformly deposited. The active anode materials were deposited in 3D on these substrates. Cross sectional analysis of these samples show

uniform deposition on Ni structures. Li storage results of the deposited films show a significant increase in surface area for 3D substrates with capacities a factor of 2.6 times that of the planar ITO. Sequential deposition of all battery materials and full cell assembly is under progress.

Acknowledgment.

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References

1. J.W. Long, B. Dunn, D.R. Rolison, H.S. White, Chem. Rev. 104 (2004) 4463.
2. C. Navone, J.P. Pereira-Ramos, R. Baddour-Hadjean, R. Salot, J. Power Sources 146 (2005) 327.
3. C. Wang, L. Taherabadi, G. Jia, M. Madou, Y. Yeh, B. Dunn, Electrochem. Solid State Lett. 7 (2004) A435.
4. D. Golodnitsky, V. Yufit, M. Nathan, I. Shechtman, T. Ripenbein, E. Strauss, S. Menkin, E. Peled, J. Power Sources 153 (2006) 281.
5. H.S. Min, B.Y. Park, L. Taherabadi, C. Wang , Y. Yeh, R. Zaouk, M.J. Madou, B. Dunn, J. Power Sources 178 (2008) 795.
6. S. Passerini, J. Scarminio, B. Scrosati, D. Zane, F. Decker, J. Appl. Electrochem. 23 (1993) 1187.
7. W.H. Ho, C.F. Li, H.C. Liu, S.K. Yen, J. Power Sources 175 (2008) 897.

8. T. Brousse, R. Retoux, U, Herterich, D.M. Schleich, J. Electrochem. Soc. 145 (1998) 1.
9. I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2943.

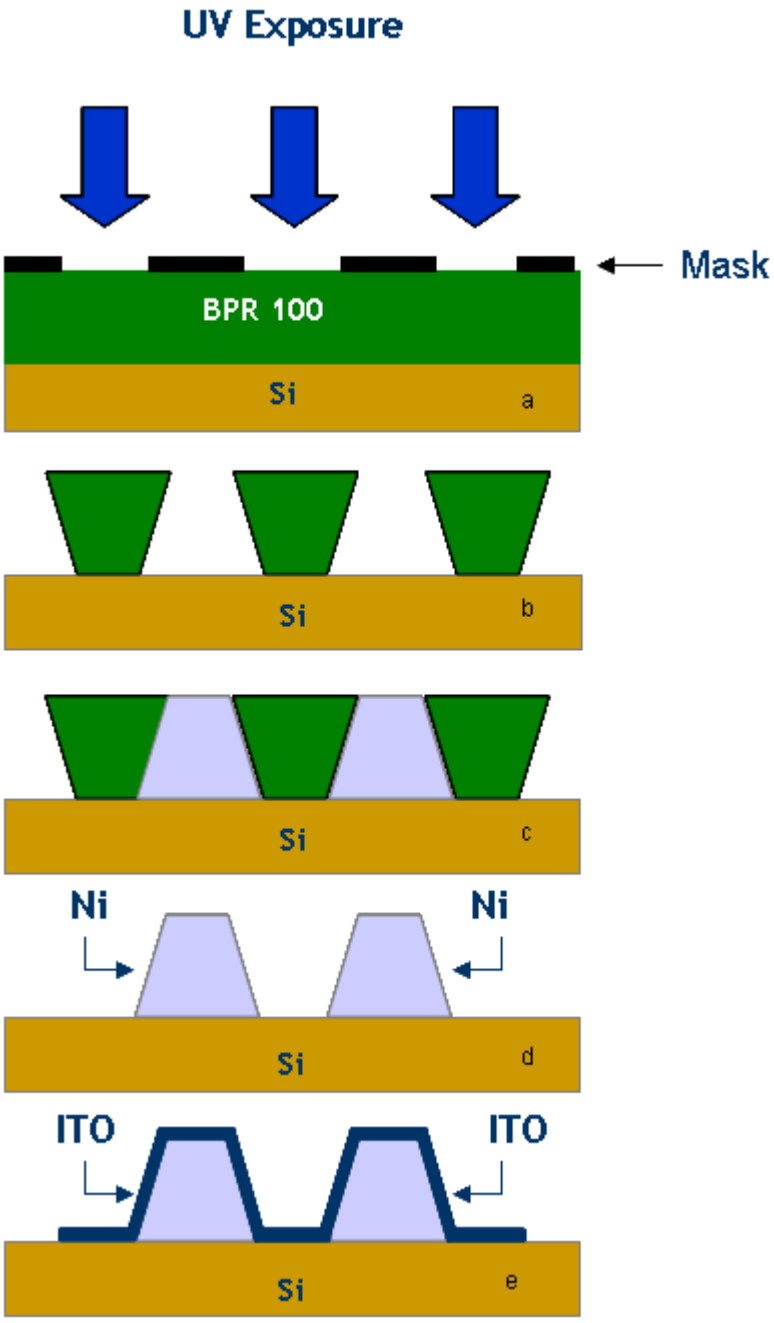
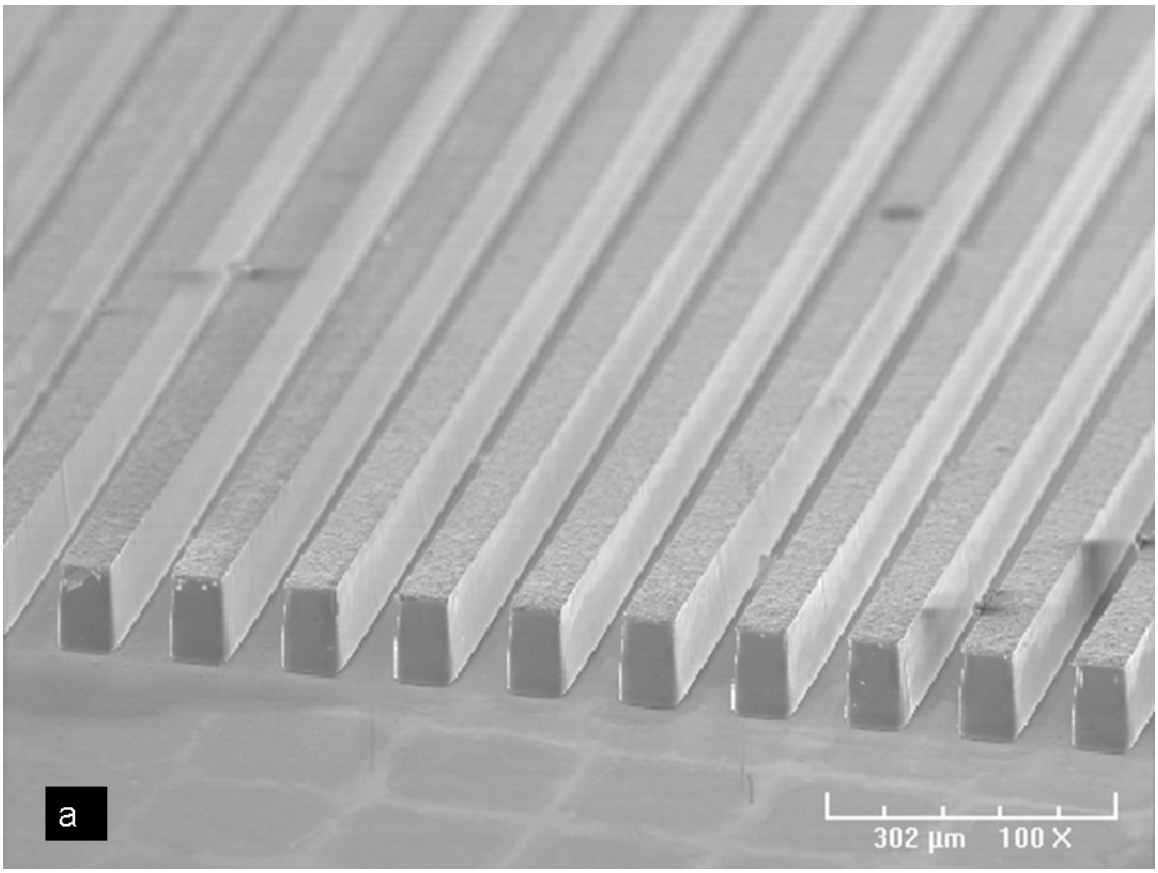


Fig. 1. Schematic of photolithographic patterning process and Ni microstructuring. (a) Spin a layer of photoresist and UV expose (b) develop the photoresist (c) Electroplate Ni (d) Remove remaining photoresist (e) Evaporation of ITO on Ni microstructure.


a
302 µm 100 X

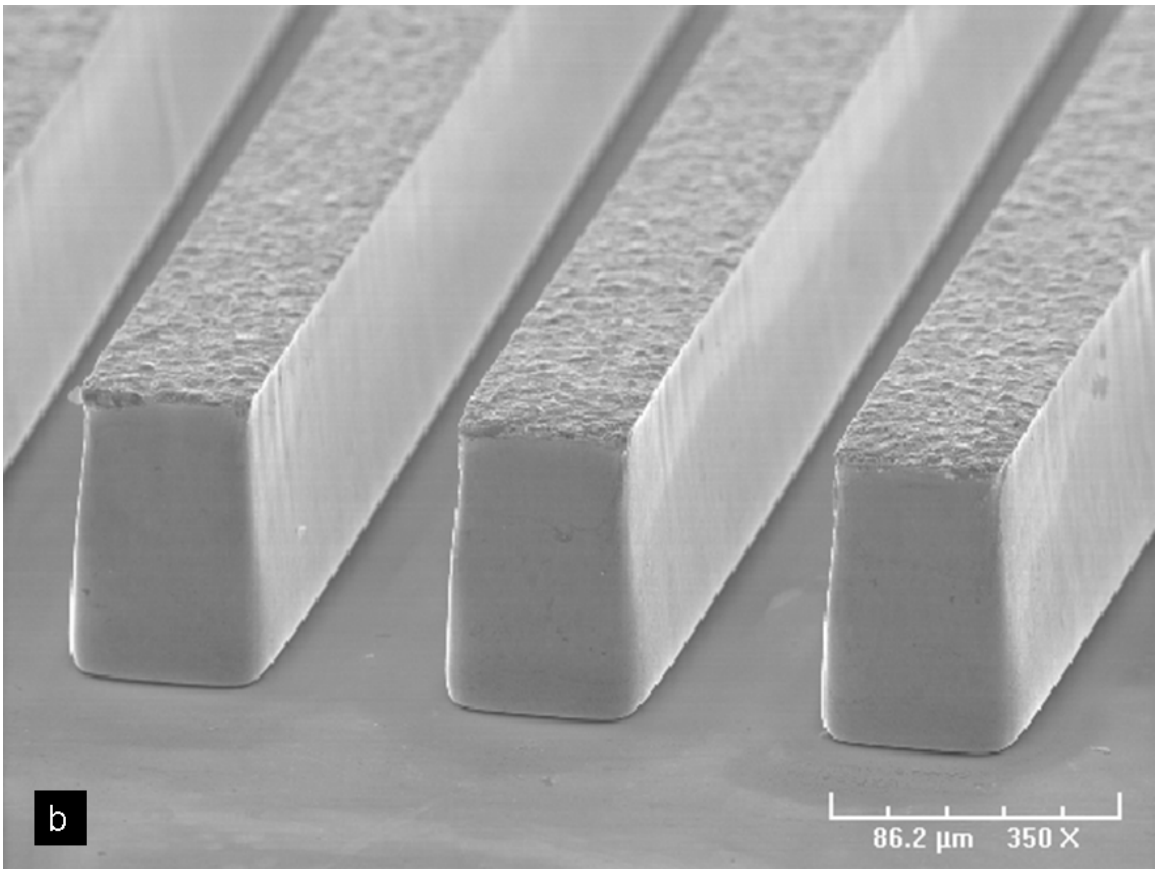


Fig. 2. (a) Electroplated Ni microstructure on Si wafer (b) 60 µm Ni lines and 60 µm gap.

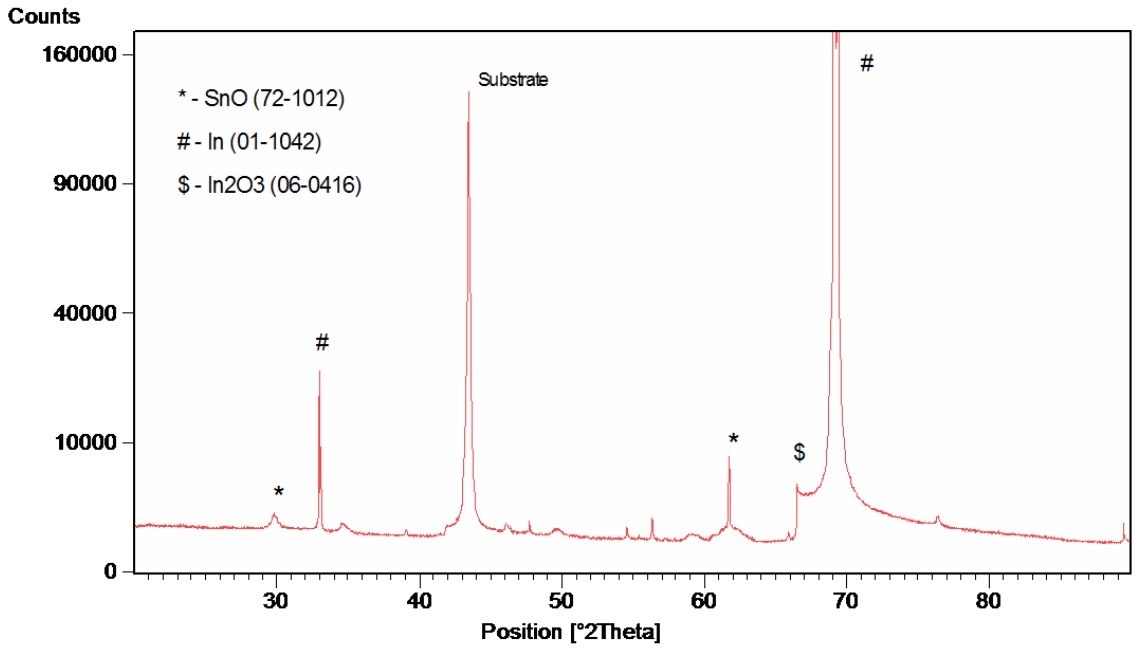
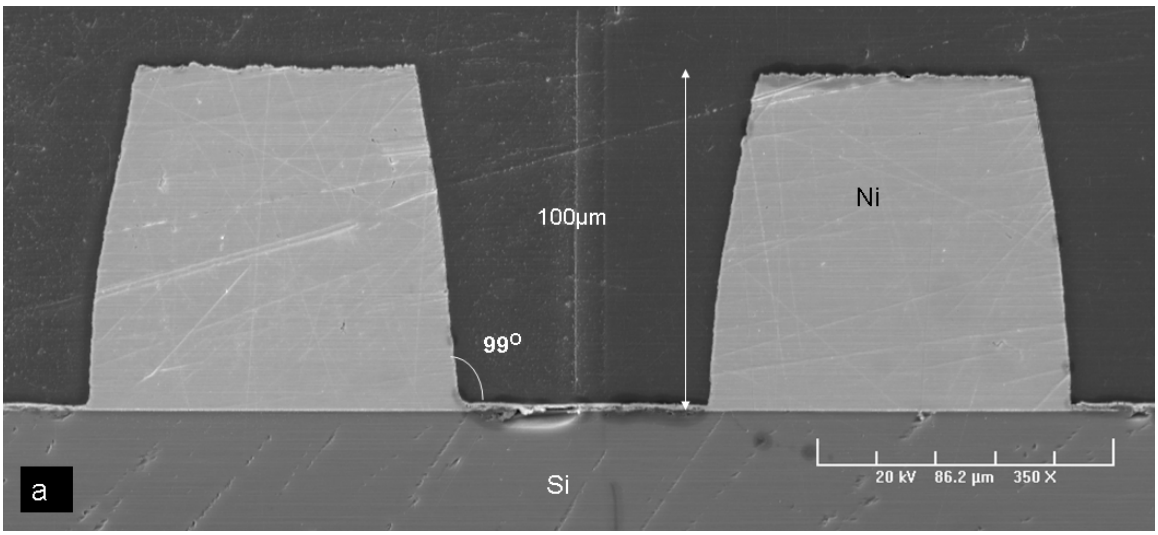
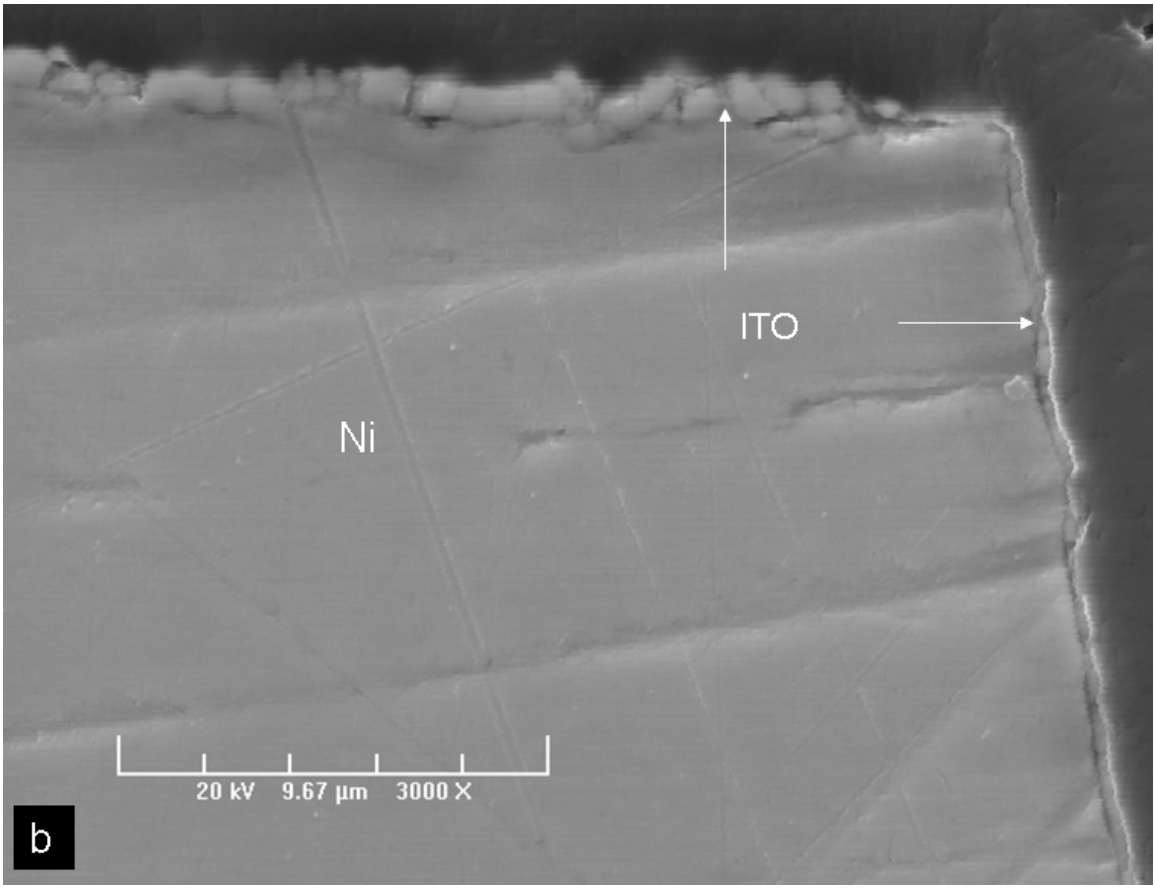


Fig. 3. X-Ray diffractogram of 1 µm thick planar ITO deposited on Si wafer




ITO
Ni
20 kV 9.67 µm 3000 X
b

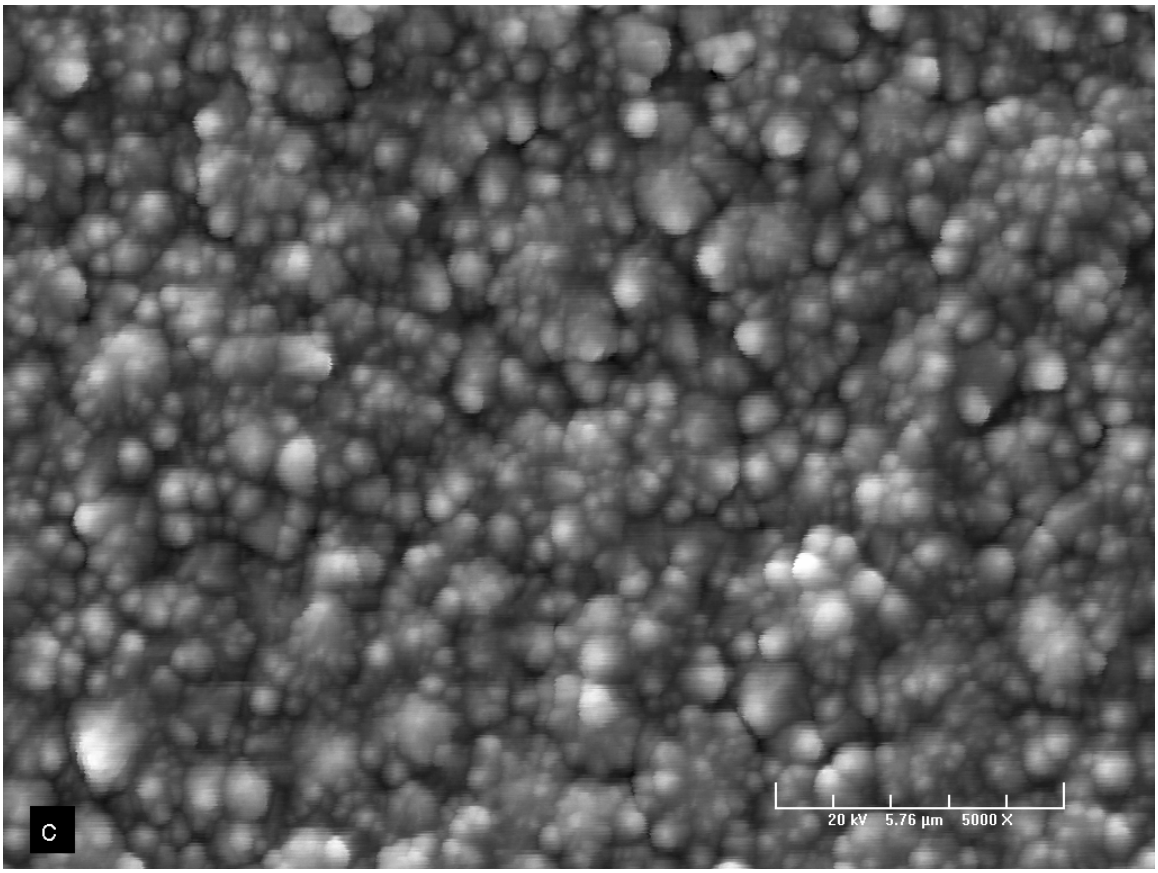


Fig. 4. (a) Cross sectional SEM image of ITO deposits on Ni microstructured lines, magnification 350X. (b) Higher magnification SEM image, magnification 3000X (c) Plan SEM image of as-deposited ITO film on Ni/Ti/Si wafer, magnification 5000X

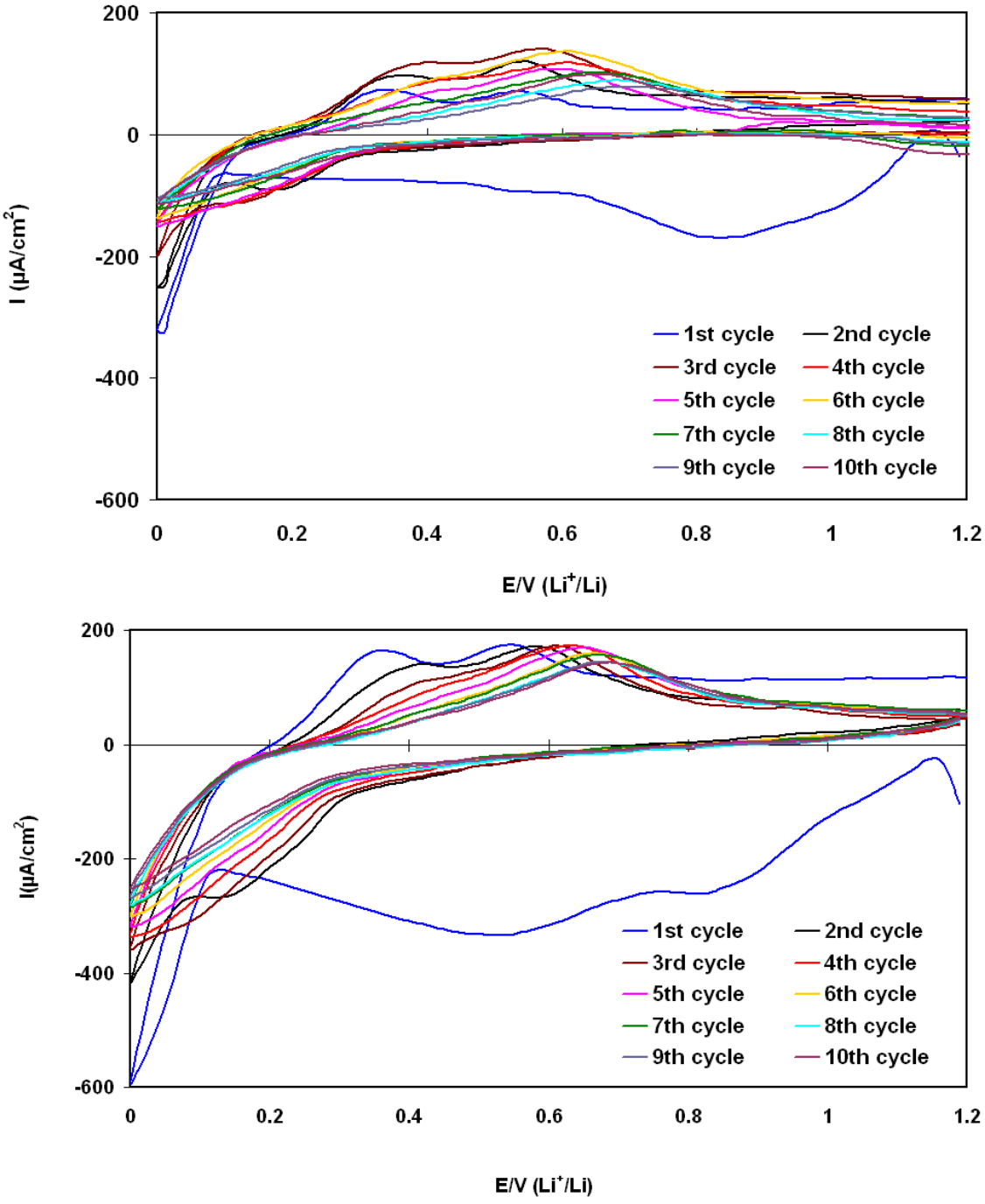


Fig 5 Cyclic voltammograms of 1 µm thick ITO films (+1.2 to 0.0 V vs. Li^+/Li) at 0.5 mV/s on (a) planar substrate and (b) over 3D Ni microstructured features (80 µm lines)

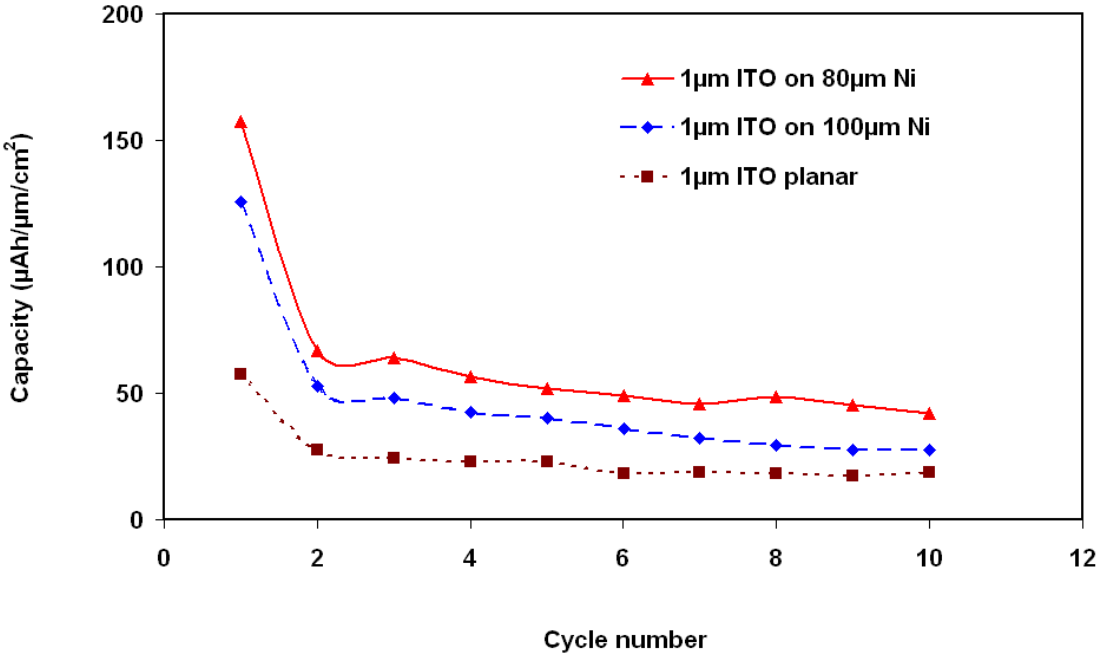


Fig 6. Capacity values of Li storage in ITO on planar and 3D Ni microstructures.