Solid-State Dewetting and Pt-$SrTiO_3$ Interfaces

Galit Atiya[1], Anna Altberg[1], V. Mikhelashvili[2], Gadi Eisenstein[2], and Wayne D. Kaplan[1]

[1]Department of Materials Science & Engineering , [2]Department of Electrical Engineering, Technion – Israel Institute of Technology, Haifa, Israel

Introduction

- *Solid-state dewetting has become a common method for "bottom-up" processing , such as for producing catalyst particles and nanocrystals (NCs) for memory devices. [1-3]*
- *$SrTiO_3$ has a cubic perovskite structure and excellent dielectric (band gap ~3.2eV) ferroelectric and optical properties for microelectronics applications.[4]*
- *Non-volatile memory (NVM) transistors and capacitors which use Pt nanocrystals (NC) for charge storage shows very good electrical properties such as: memory window, trapped charge density etc.[5]*
- *$SrTiO_3$ is composed of SrO and TiO_2 atomic planes (figure 1) in the <100> direction, a TiO_2 terminated surface was found to be energetically favorable over a SrO terminated surface [6-7] .*
- *TiO_2 termination is achieved by BHF solution which selectively dissolved the SrO atomic plane followed by high temperature annealing. (figure 2).*
- *Pt-$SrTiO_3$(100) orientation relationships were reported by A.D. Polli et al. [8] after annealing in UHV:*
  - *TiO_2 termination -$[01\bar{1}](100)Pt\|\|[011](100)SrTiO_3$*
  - *SrO termination – $[01\bar{1}](111)Pt\|\|[011](100)SrTiO_3$*

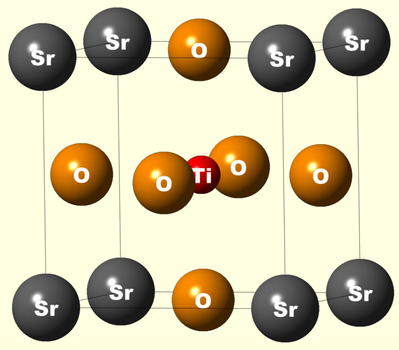

Figure 1: Schematic drawing of the $SrTiO_3$ perovskite structure showing the SrO and TiO_2 atomic planes in the [100] direction.

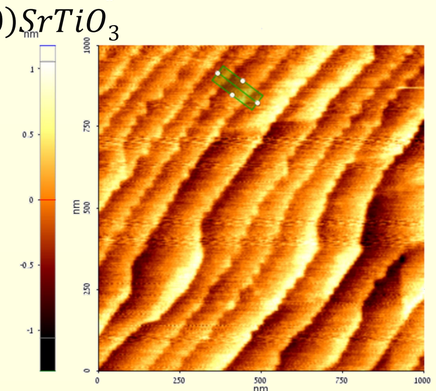

Figure 2: AFM image of an BHF etched substrate surface followed by annealing at 950˚ for 2hr in air.

Experimental Procedures

(100) $SrTiO_3$ single crystal ($10X10X0.5mm^3$) (miscut< 0.5˚) → Buffered NH_4F-HF (BHF) solution for 1 min, (fig. 2) → A 50 nm thick Pt deposition by evaporation (Pt: 99.99% pure , deposition rate ~0.1-0.2Å/sec) → Annealing in $Ar+H_2$ or $Ar+O_2$ at 1150˚C (fig. 3)

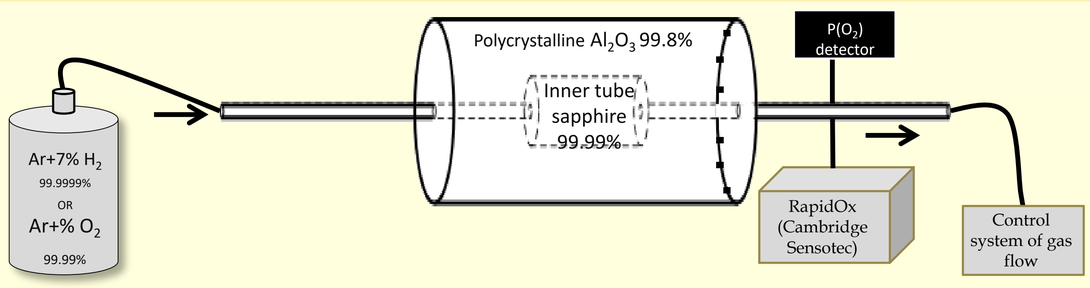

Figure 3: Schematic drawing of the furnace which provides a controlled oxygen partial pressure during annealing (dewetting).

Results and Discussion

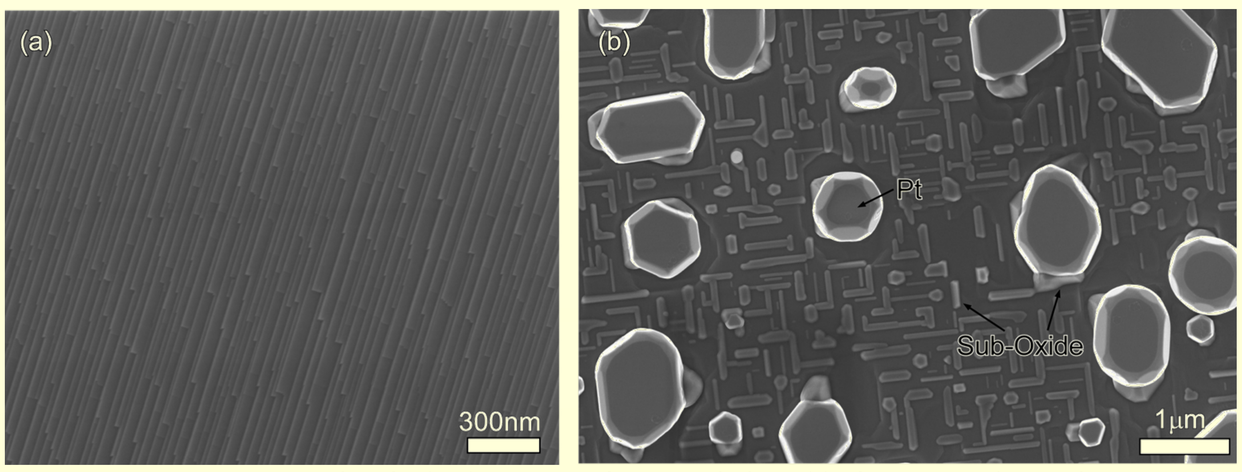

Figure 4: HRSEM micrographs of a (100) $SrTiO_3$ surface morphology (a) after BHF and annealing at 1150˚C in $Ar+H_2$ ($P(O_2)$~10^{-25}atm) for 2hr (b) dewetted Pt particles and reduced substrate annealed at 1150˚C in $Ar+H_2$ ($P(O_2)$~10^{-25}atm) for 10hr.

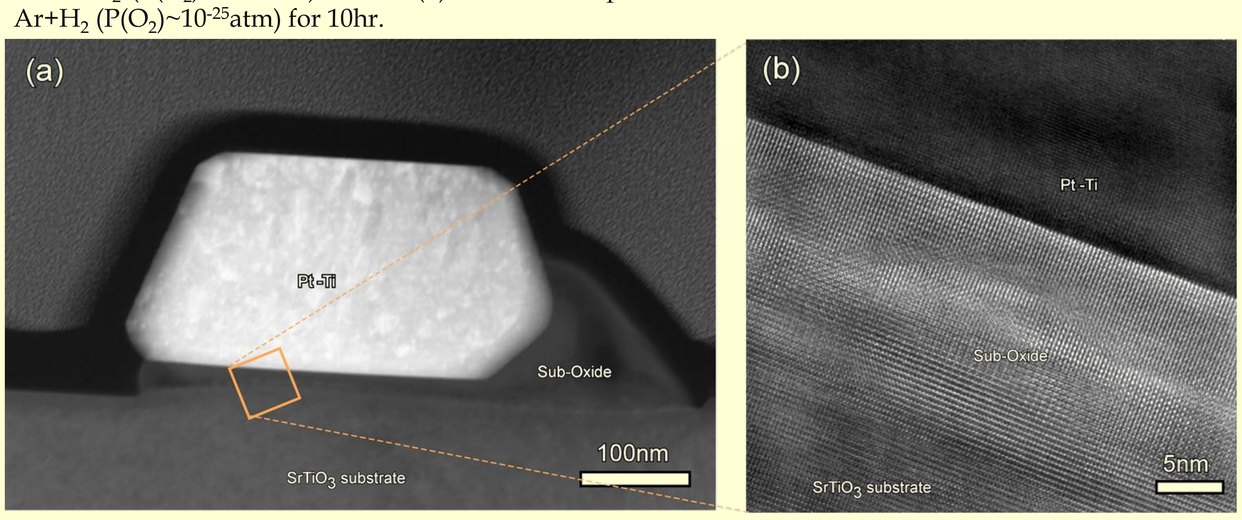

Figure 5: (a) HAADF micrograph of a dewetted particle. (b) Cs corrected HRTEM micrograph of the interface between the $SrTiO_3$ substrate and a Pt particle shows the sub-oxide layer. Corresponding FFT of the *reconstructed exit wave* of (c) Pt particle (d) sub-oxide layer shows tetragonal distortion in $[100]_{SrTiO_3}$ direction (~8.5%) and additional spotd at the middle of $[011]_{SrTiO_3}$ direction. (e) $SrTiO_3$ substrate annealed at 1150˚C in $Ar+H_2$ ($P(O_2)$~10^{-25}atm for 10hr.

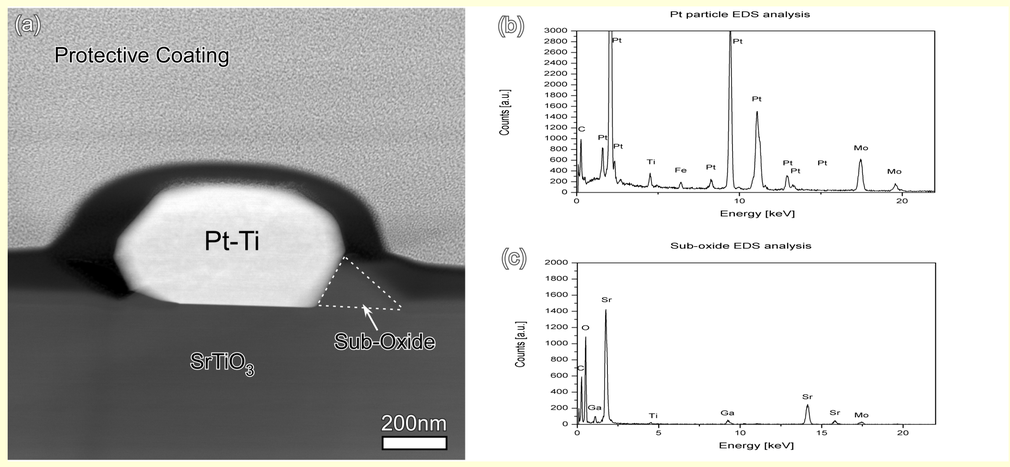

Figure 6: (a) HAADF micrograph of a dewetted particle and (b) EDS analysis results show that Pt particles contain a small amount of Ti. (c) EDS analysis from the sub-oxide layer show the presence of only Sr and O.

Different Partial Pressures of Oxygen

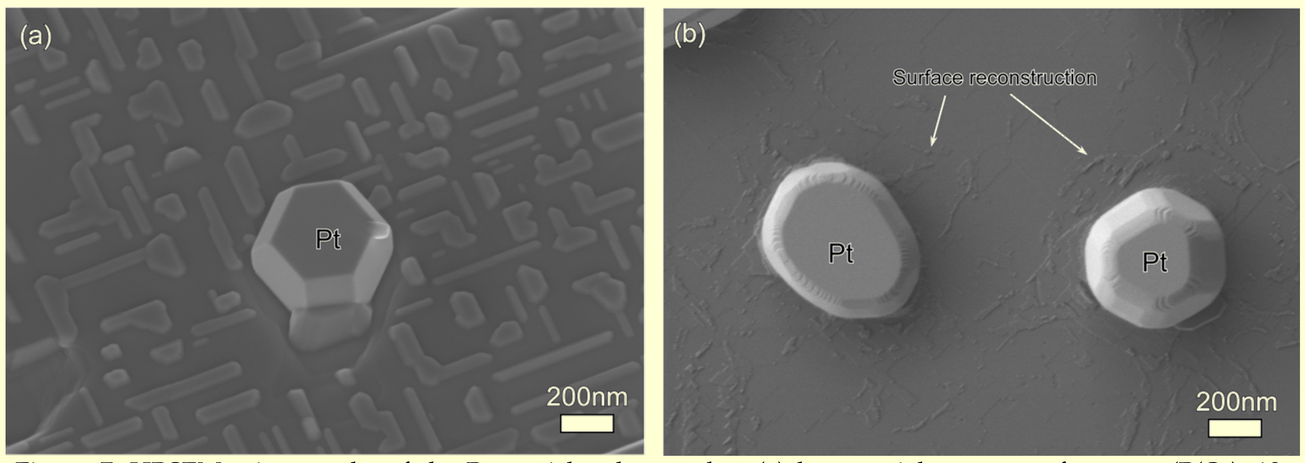

Figure 7: HRSEM micrographs of the Pt particles dewetted at (a) low partial pressure of oxygen ($P(O_2)$~10^{-25}atm) (b) high partial pressure of oxygen ($P(O_2)$~10^{-2}atm). annealed at 1150˚C for 10hr.

- *Fig. 4a and 4b show the annealed $SrTiO_3$ (100) substrate with TiO_2 termination and the annealed $SrTiO_3$ (100) substrate with TiO_2 termination coated with a thin Pt film (~50nm), respectively. In addition to equilibrated Pt particles (fig. 4b), anisotropic lateral features were visible on the surface of the substrate and at the interface while the bare $SrTiO_3$ the surface is composed of ~30-70nm terraces(fig. 4a). These results imply that the Pt serves as a catalyst which reduces the $SrTiO_3$.*
- *HRTEM analysis with corresponding FFT of the reconstructed exit wave (fig. 5) show that Pt (111) is parallel to the $SrTiO_3$ (100) substrate and not Pt(100) as expected due to the small lattice mismatch (~0.4%). This indicates that the interfacial energy of Pt(100) and the sub-oxide is higher than Pt(111).*
- *These results contradict previous research done by Polli et al. [R] who reported that Pt(100) is parallel to $SrTiO_3$ (100). The difference can be explained by the different annealing atmospheres and temperatures which probably caused different surface reconstruction of the $SrTiO_3$ (100), leading to different low energy interface states.*
- *EDS analysis of the sub-oxide layer was conducted using $SrTiO_3$ (100) as an internal standard. K factors were determined from intensity ratios. EDS measurements from the sub-oxide revealed that there is no Ti, however a small amount of Ti was found in the Pt particle. This indicates that Ti diffuses into the Pt during dewetting and a sub-oxide (free from Ti) is created by reduction. The sub-oxide was found to be SrO_x (x=3-4), but because of a large standard deviation (probably due to the effect of specimen thickness) EELS analysis needs to be done to determine the exact concentration.*
- *Fig. 7b shows that under high oxygen partial pressure no surface reduction occurred. However, the Pt particle shape is not fully faceted, it can be correlate to oxygen adsorption which may influence the anisotropy of surface energies.*

References

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