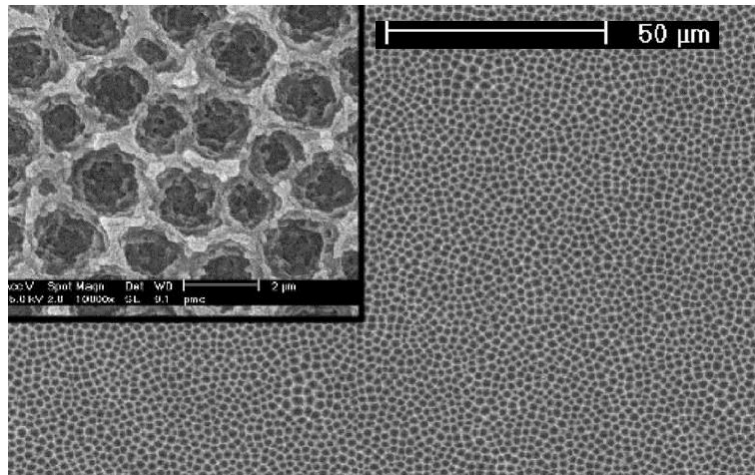


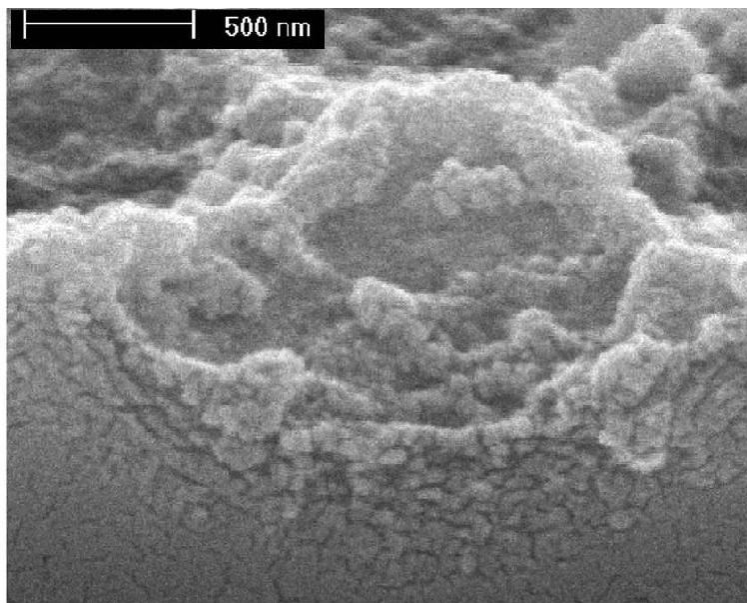
Microcracking in Anodic Oxides on Si

Advanced

- Let's do an extremely simple experiment that produces a "thin film" with quite mysterious properties:
 - We take a piece of **Si** and immerse it into some electrolyte that can only react with the **Si** by forming **SiO₂**; acetic acid or (diluted) **HNO₃** or whatever, will be fine in principle.
 - Now we take a big power supply (a "galvanostat") and run a constant (anodic) current through the **Si** - electrolyte interface. The necessary chemical reaction occurring is the formation of **SiO₂** - nothing else is possible.
 - So we start to build up a thin layer of **SiO₂** on top of the **Si** substrate. But **SiO₂** is an insulator, so it will impede current flow. Our power supply must keep the current constant, so it will crank up the voltage as the **SiO₂** layer gets thicker. Eventually, the voltage will go to infinity.... ?
- Interestingly, this is *not* what happens. The voltage will go up in the first few minutes or so, but then it will stay more or less constant. The thickness of the **SiO₂** layer formed, will also stay more or less constant. Moreover, it will, on occasion, form interesting self-organized structures as shown below. Now we have a puzzle!
- First we have to realize that the **SiO₂** layer will be under tremendous compressive stress. Why, you might ask. The temperature, after all, is room temperature and constant throughout the experiment.
 - Well, when a certain volume of **Si** is oxidized, you essentially put an oxygen atom in between two **Si** atoms. In consequence, if you oxidize **1 cm³** of **Si**, you get almost **2 cm³** of oxide. Since the oxide film being formed cannot expand in lateral directions, and is perfectly brittle at room temperature, a very large compressive stress builds up rather quickly. At a thickness of about **12 nm** it is so large that something must happen; the thickness just can't go up very much anymore.
 - On the other hand, as long as a constant current flows through the interface, we are producing oxide at a constant rate. The thickness thus should increase linearly with time.
- "Obviously", we must have a mechanism that allows to get rid of oxide at the same rate it is being formed so the thickness can stay halfway constant.
 - Any suggestions? The best, researchers could come up with so far is that the oxide "cracks off" somehow. But nobody really knows how that is supposed to happen.



"Thin" layer of anodically formed oxide on **Si**. Not the self-organized pattern and the "grainy" structure of the oxide



Cross-section through on "dimple". The interface between the **Si** and the **SiO₂** is not visible; it is somewhere at the bottom of the picture. Note the "microcracks"

S. Frey, B. Grésillon, F. Ozanam, J.-N. Chazalviel, J. Carstensen, H. Föll, and R.B. Wehrspohn,
"Self-Organized Macrostructures in anodically formed mesoporous silica",
Electrochem. Sol. State Lett. 8(9), B25 (2005).