How Nanoscale Substrate Properties Influence the Growth of VO_2 Single Crystals

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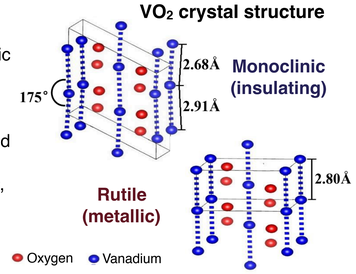
Why VO_2 Single Crystals?

- **Metal-insulator transition** at ~68°C[1]
  - Structural AND electronic
  - Induced thermally or optically
- **Applications** in physics and engineering
  - Optoelectronic switches, smart windows[2,3]
  - Optical physics experiments

VO_2 crystal structure



Substrate Physics

What properties of substrate affect crystal properties?

1. Thermal expansion

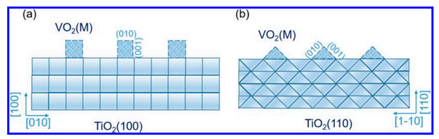
- Different thermal expansion coefficients —> Crystals strained during heating/cooling—> metal insulator stripes[4]

2. Surface chemistry

- Vanadium oxides react with substrate surface
  - Creation of byproducts
  - Corrosion

3. Lattice Match

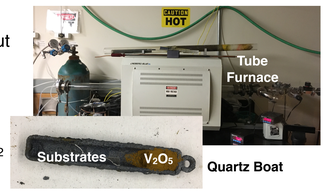
- Preferred orientation
- Evidence of epitaxy



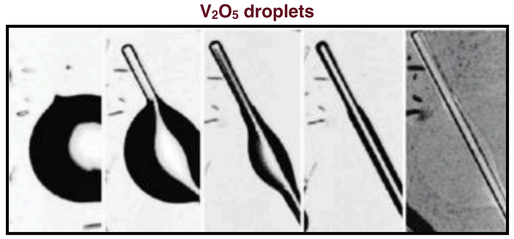
Representation of VO_2 crystal growth crystal structure of substrate[5]

Vapor Transport Growth

1. V_2O_5 powder in quartz boat with substrates put into furnace
2. Powder vaporizes and condenses onto substrate
3. Loses oxygen and VO_2 crystallizes

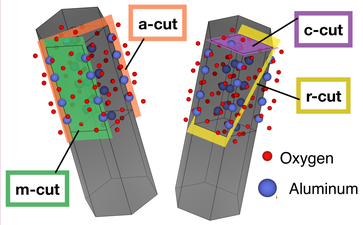


Growth Mechanism: VO_2 crystals form from liquid V_2O_5 droplets



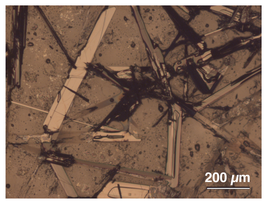
Images of crystals growing out of droplets by Strelcov et al.[6]

Sapphire (Al_2O_3)

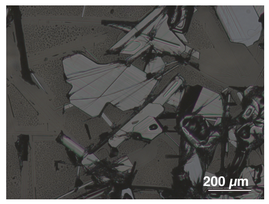


Hexagonal crystal structure of sapphire and lattice planes at surface of different cuts of sapphire

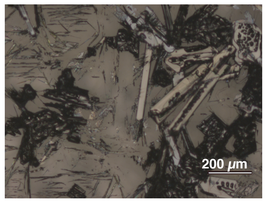
c-cut (0001)



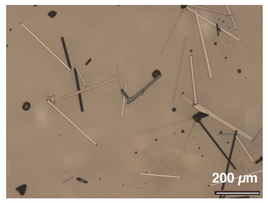
r-cut ($1\bar{1}02$)



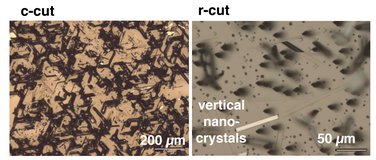
m-cut ($10\bar{1}0$)



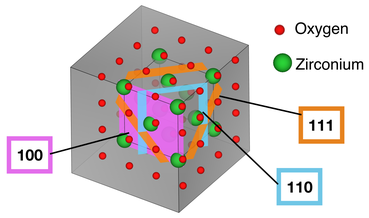
a-cut ($11\bar{2}0$)



- Most crystals in **M2 phase**:
  - EDX shows aluminum doping which is known to stabilize M2[7]
- Dark, rough material forms on substrate and crystals, possibly due to reaction
- **Preferred orientation**
  - 60° angles between crystals on c-cut sapphire
  - **Vertical crystals** on r-cut

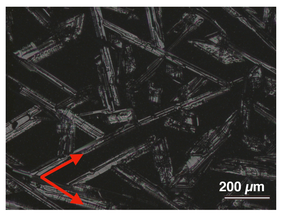


Yitrium Stabilized Zirconia (YSZ)

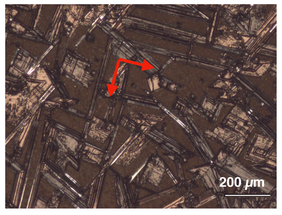


Cubic ZrO_2 structure (stabilized by Y impurities) and lattice planes at surface of different cuts of YSZ

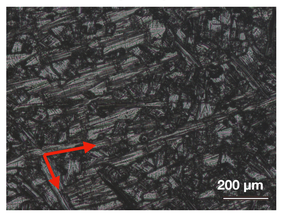
(111)

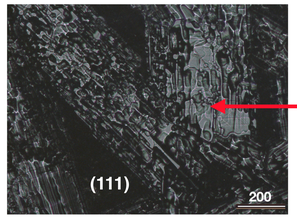


(100)



(110)



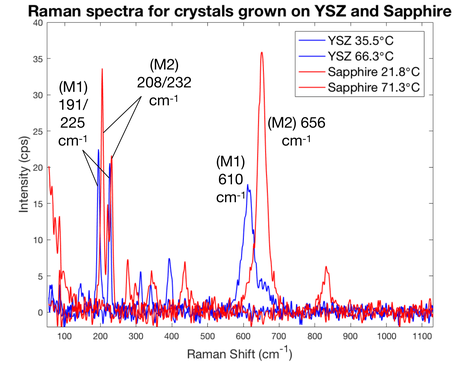


- Evidence of **preferred orientation** (indicated with red arrows), especially on (100)
- VO_2 on top of **YVO_4 film** grows on YSZ (confirmed by Raman)[8]
- All cuts yield large crystals with rough surface texture

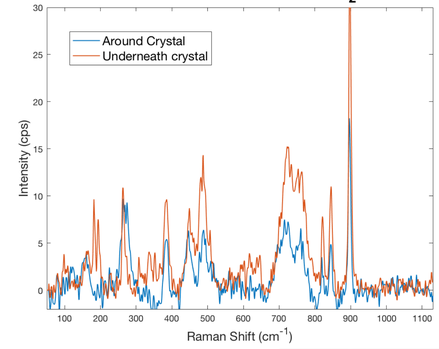
*All images taken with polarized optical microscope

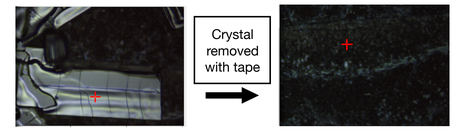
Raman Spectroscopy demonstrates effects of surface chemistry

Raman spectra for crystals grown on YSZ and Sapphire



Raman spectra for dark film on YSZ after VO_2 crystal growth





(Top) Raman spectra showing M2 phase in crystals grown on sapphire and M1 in crystals grown on YSZ. Lack of peaks at high temperature indicates rutile structure. (Bottom) Spectra from material formed on YSZ substrate around and under a crystal. Indicates formation of YVO_4 layer.

Conclusions

- Lattice match affects **preferred growth orientation**
  - YSZ and sapphire produce different morphologies
  - Different orientation depending on cut of substrate
- **Chemical interactions** between vanadium and substrate affect crystals– *complicate our understanding* of growth mechanism/lattice matching
  - Thin film of YVO_4 forms between YSZ and sapphire crystals
  - Aluminum doping of sapphire crystals possibly due to corrosion
- Paves the way for applications of VO_2 crystals in optical experiments
  - Image phonon polaritons in hexagonal boron nitride deposited on VO_2 crystals[9]

References

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[6]Strelcov, E. et al. "In situ monitoring of the growth, intermediate phase transformations and templating of single crystal VO_2 nanowires and nanoplatelets"(2011). *ACS Nano*, *5*(4), 3373–3384.

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Note: Figures showing crystal lattice structures made using VESTA.

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