# Temperature induced morpho-structural and electronic changes of $MoO_3$ thin films

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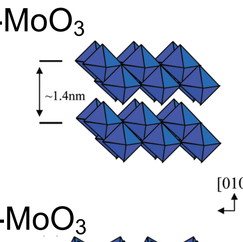
## Abstract

- Transition metal oxide $MoO_3$ is widely applied in photovoltaic as well as optoelectronic devices [1].
- The temperature induced change in work function and structure of 15 nm $MoO_3$ have been investigated by Kelvin probe force microscopy and Raman spectroscopy.
- The work function of $MoO_3$ increasees with increasing annealing temperature, which is related to the oxygen vacancies and structure.

## Motivation

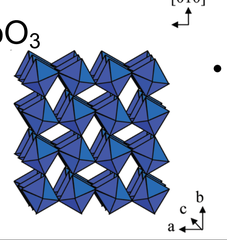
### Physical properties of $MoO_3$

$\alpha$-$MoO_3$




- Thermodynamically stable orthorhombic **$\alpha$-$MoO_3$** [2]
  : Octahedral $MoO_6$ forms corner sharing rows along the [100] planes and edge-sharing zigzag rows along [001] planes.
  : Reduction in the number of layers can increase the carrier mobility.

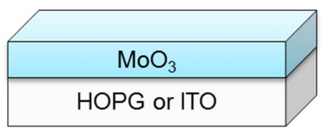
$\beta$-$MoO_3$




- Metastable monoclinic **$\beta$-$MoO_3$** [2]
  : Adjacent octahedral $MoO_6$ shares corners in three dimensions to produce a monoclinic structure.

## Experimental

### Thin-film Preparation

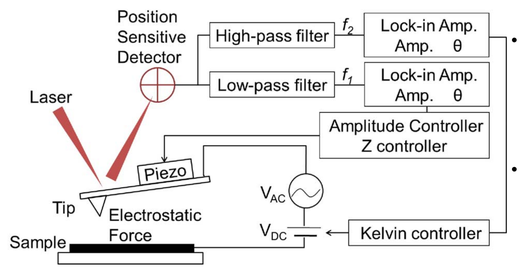



- $MoO_{3-x}$ as hole transport layer by PVD in high vacuum (~$10^{-7}$ mbar)
- Substrates :
  Highly Ordered Pyrolytic Graphite (HOPG),
  glass / Indium tin oxide (ITO), quartz glass

### Characterization

- Work function by ultra high vacuum Kelvin probe force microscopy (UHV-KPFM (~$10^{-10}$ mbar))
- Structure by Raman spectroscopy (488 nm laser, 3.0 mW, in ambient)
- Chemical states by XPS and XAS (UHV (~$10^{-9}$ mbar))

#### *Ultra-high vacuum (UHV) KPFM*

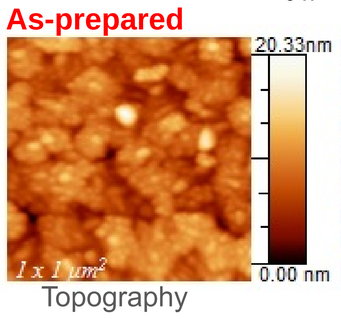



- Work function of the sample measurement by KPFM
  $\Phi_{sample} = \Phi_{tip} + eV_{CPD}$
  ($e$ : elementary charge, $V_{CPD}$ : contact potential difference )
- Sample transport from $N_2$ filled glove box to UHV KPFM (~ $10^{-10}$ mbar) without air exposure

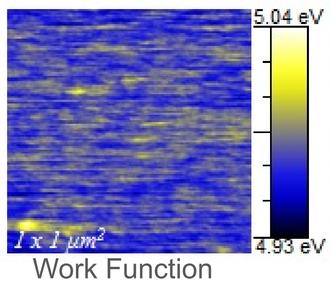
## Morphology and Electronic Properties of $MoO_{3-x}$

♦ ITO / 15 nm $MoO_{3-x}$

**As-prepared**

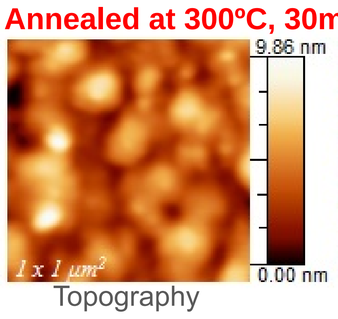


Topography



Work Function

**Annealed at 300ºC, 30min**



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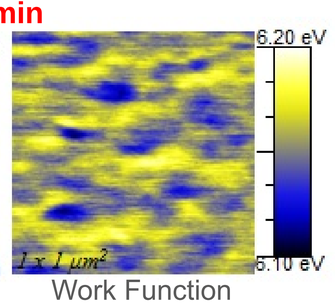
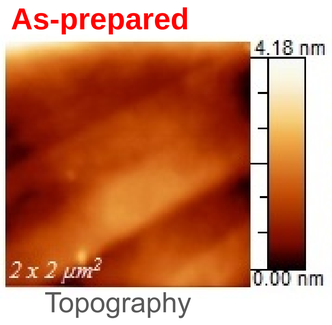


Work Function

♦ HOPG / 15 nm $MoO_{3-x}$

**As-prepared**



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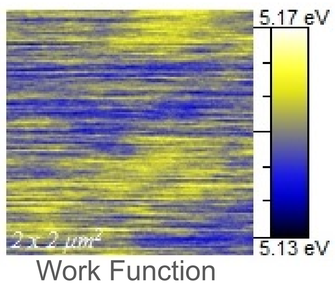
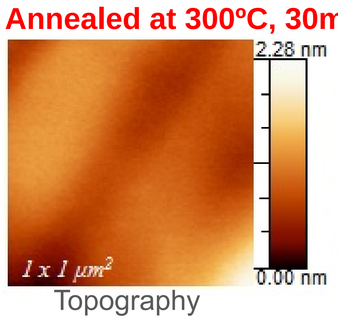


Work Function

**Annealed at 300ºC, 30min**



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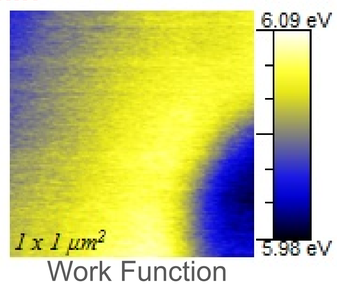


Work Function

### KPFM analysis

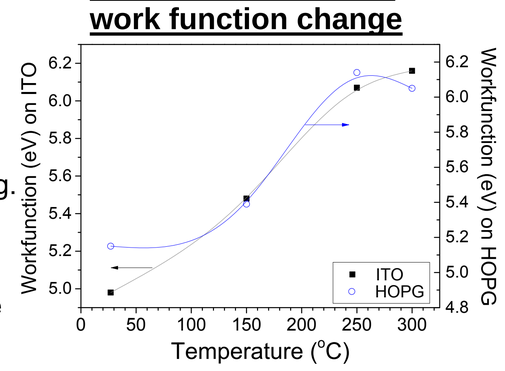
| $MoO_{3-x}$ on / Annealing temperature | ITO | | **$MoO_{3-x}$** on **HOPG** | |
|---|---|---|---|---|
| | Work function (eV) | RMS roughness (nm) | Work function (eV) | RMS roughness (nm) |
| As-prepared | 4.98 ± 0.01 | 2.4 | 5.15 ± 0.02 | 0.2 |
| 150°C | 5.48 ± 0 01 | 1.5 | 5.39 ± 0.01 | 0.6 |
| 250°C | 6.07 ± 0.02 | 1.6 | 6.18 ± 0.01 | 0.2 |
| 300°C | 6.16 ± 0.01 | 1.5 | 6.05 ± 0.01 | 0.3 |

- Temperature induces work function increases regardless of the substrates.

### XPS analysis

: Oxygen vacancies are created by annealing.
$Mo^{6+}$ (30°C) → $Mo^{5+}$/$Mo^{4+}$ (310°C).
⇒ Oxygen vacancies can influence not only work function but also distort of the structure[3].

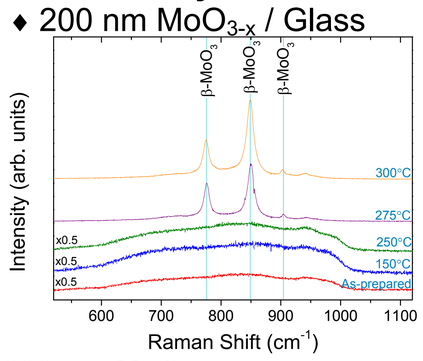
**Temperature induced work function change**



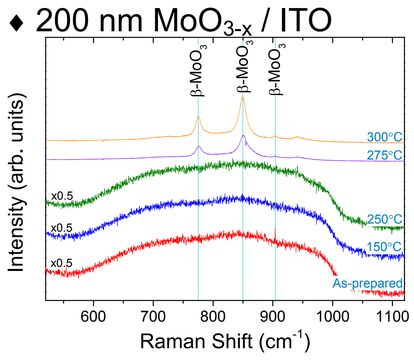

## Structural Properties of $MoO_{3-x}$

### Raman analysis

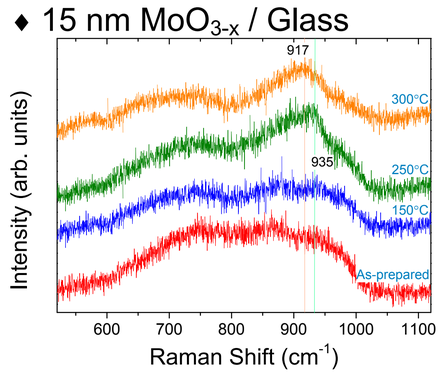
♦ 200 nm $MoO_{3-x}$ / Glass



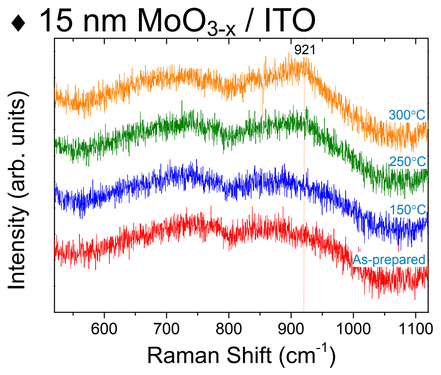

♦ 200 nm $MoO_{3-x}$ / ITO



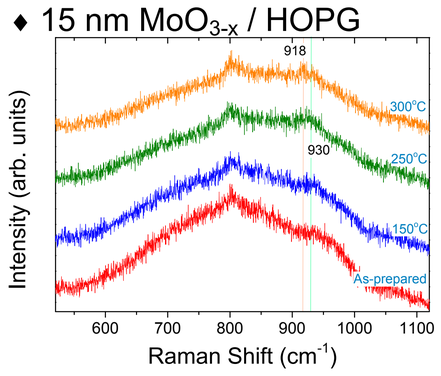

♦ 15 nm $MoO_{3-x}$ / Glass




♦ 15 nm $MoO_{3-x}$ / ITO




♦ 15 nm $MoO_{3-x}$ / HOPG




**200 nm $MoO_{3-x}$**

- Temperature-induced transformation of crystal structure in $MoO_3$ : amorphous → $\beta$-phase [2,4]
- Raman spectra show the phase change of 200 nm $MoO_3$ from amorphous to $\beta$-phase after annealing above 275°C.

**15 nm $MoO_{3-x}$**

- The broad signal from 800 to 1020 $cm^{-1}$ is related to the $MoO_3$ frame [5].
- Increase of Raman band at 917, 935, 921, 918, 930 $cm^{-1}$ indicates crystallization by annealing above 250°C.
- It is clearly shown that crystallinity on 15 nm $MoO_{3-x}$ is induced by annealing.
- Increase of Raman line width :
  probably formation of nano-crystallinities in amorphous matrix and/or strain induced distortion of crystal structure [6].

### XAS analysis

: Presence of distorted octahedral $MoO_6$ (before annealing) and $MoO_2$ (after annealing at 310°C) in $MoO_3$. → Oxygen vacancies can influence degree of distortion and change the crystallinity.

## Conclusion

- Temperature induced change in the electronic, crystal, and chemical structure of $MoO_{3-x}$ has been investigated.
- Annealing in UHV increases the work function regardless of substrates.
- 15 nm $MoO_{3-x}$ shows structural changes after annealing over 250°C, which is correlated with the work function change of the layer.

### References

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