Nanoparticle generation using sputtering plasmas

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synthesis & characterization materials plasmas
HiPIMS – an important theme for some years.
Moving Ionization Zones

- Nb discharge, peak $\sim 200$ A
- reduction of image exposure time gives immediate clues on rotational speed $\Rightarrow \sim 10^4$ m/s

Streak image sequence, 20 μs sweep time

Perhaps the first observation of nanoparticles

“The black dust was so extremely light as to rise like a cloud in the air, so as sometimes to be visible near the top of the room; I concluded that it could not be the metal itself, but probably the calx [oxide], ....I was confirmed in this opinion by finding that this black dust collected from a brass chain would not conduct electricity...” (J. Priestley, 1775)

Interesting for energy related applications:
- Transparent in visible and near infrared ranges
- High electrical conductivity

Other metal oxides of interest:
- VO$_2$ : thermochromic material: Metal-to-insulator transition (MIT) at 68 °C
- TiO$_2$ : Wide band-gap semiconductor, catalysis applications
- WO$_3$ : electrochromic material
Localized Surface Plasmon Resonance

Resonance: frequency of field is equal to plasma frequency of free electrons

Resonance is size-dependent
Metal vs. TCO Nanoparticles as Plasmonic Materials

Extinction (arb. units)

Solar Spectral Irradiance AM1.5 (W m\(^{-2}\) nm\(^{-1}\))

Wavelength (nm)

Al, Ag, Au, Cu, RuO\(_2\)

AZO increasing concentration of carriers

n = 0.5 - 10 \times 10^{20} \text{ cm}^{-3}

ITO
Some Applications of Nanostructured Oxides

Smart Windows

Solar heat
(infrared radiation)

Visible light

Ultimate Goal:
independent switching in the visible and infrared ranges

Photovoltaic and Photocatalytic devices

H. A. Atwater and A. Polman, Nat. Mater. 9 (2010) 205.
Approach: Terminated Cluster Growth

Source: Mantis Deposition LTD
Terminated Cluster Growth Setup

Nanoparticle generator integrated in a sputtering process chamber: option to combine nanoparticles and thin film in devices
Nanoparticle Generator

- differential pumping port
- cooling
- magnetron gun
- aggregation zone
- aperture
- nanoparticle beam

Source: Mantis Deposition LTD
Effect of Density of Nucleation and Growth

The nanocrystals size and production rate can be varied by controlling a number of parameters including:

- Sputtering gas flow rate
- Aggregation zone pressure
- Position of the target in the aggregation zone
- Sputtering power

Increased collision rate increases number and size and nanoparticles.
Effect of Argon and Oxygen Flows on Nanoparticle Formation

Even very small amounts of oxygen affect the outcome greatly.

Effect of Oxygen on Nanoparticle Size and Rate


→ heterogeneous nucleation is much more effective than homogenous nucleation
→ there is a very pronounced parameter window of effective oxide nanoparticle formation
Why Vanadium Oxide?

VO₂ is a thermochromic material
VO₂ nanocrystals are difficult to synthesize by solution chemistry

Low temperature
monoclinic phase
(insulating)

High temperature
rutile phase
(metallic)

68 °C
Vanadium Oxide: Very Complicated Phase Diagram


this is the desired phase
RBS: Checking the Nanoparticle Composition

Control of Morphology and Crystal Structure by Annealing

From Nanoparticles to Nanocrystals

Optimum thermal treatment ($375^\circ C < T < 500^\circ C$) → $\text{VO}_2$ nanoCRYSTALS

As deposited (amorphous $\text{VO}_2$)

After thermal treatment (crystalline $\text{VO}_2$)

Spectral Response: Demonstrate Switching

Spectral Response: Checking Change in Transmission

\[ \Delta T_\lambda = T_\lambda(25 \, ^\circ\text{C}) - T_\lambda(90 \, ^\circ\text{C}) \]

greatest optical switching happens here
Hysteresis of the Transition Temperature as a Function of Annealing

Hysteresis of Phase Transition at $\lambda = 1500$ nm
Summary & Conclusions

1. Oxide nanocrystals can have plasmonic properties; depend on free carrier concentration and size

2. Especially interesting are those that show insulator-to-metal transition, such as thermochromic VO₂

3. Demonstrated Terminated Cluster Growth as a synthesis method for VO₂ nanoparticles

4. There is a pronounced optimum of oxygen partial pressure (flow) for oxide nanoparticle synthesis
   1. even little oxygen promotes heterogeneous nucleation
   2. too much oxygen poisons the target and reduces rate

5. Demonstrated transition from nanoparticles to nanocrystals with optimum annealing temperature ~ 400°C as judged by maximum switching in the infrared (1500 nm)
1. Use pulse sputtering $\Rightarrow$ we have seen significant rate increases
2. Use in-situ annealing to obtain nanocrystals
3. Use multi-element targets and gases
4. Embed nanoparticles/crystals in a matrix and make devices
5. Scale to a linear system for large area
6. ....