Effect of Oxygen Content in Silicon Suboxide Nanoparticles on UV Radiation Shielding

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Introduction

- **Information about UV radiation**
  - ✓ Exposure from UV causes harmful damages to human health
  - ✓ UVA (315-400 nm) and UVB (280-315 nm) rays reach the ground surface unlike UVC (100-280 nm)

- **Non-stoichiometric silicon suboxide (SiO_x, $0 < x < 2$)**
  - ✓ A promising oxide material due to its high chemical stability and good mechanical properties[1]
  - ✓ Widely applied to semiconductors and optical coatings thanks to the outstanding optical properties of SiO_x
  - ✓ The inherent properties can be maximized if SiO_x forms nanostructures
  - → SiO_x nanoparticles: A good candidate for UV shielding

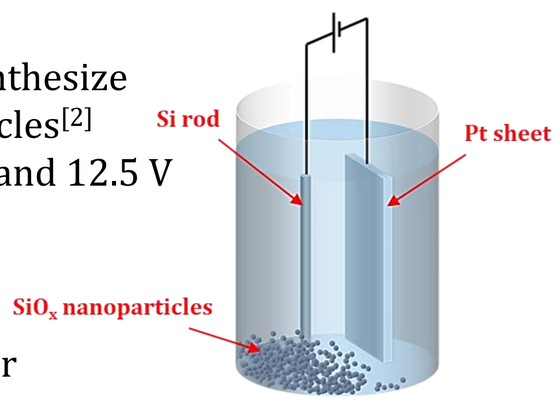
- **Effects on optical property depending on oxygen content**
  - ✓ Oxygen content is expressed as the oxidation state of a material
  - ✓ Different oxidation state means a different chemical state
  - → Resulting in changes in UV absorption or wavelength range

- **Focus of research**
  - ✓ Showing the UV shielding characteristic of SiO_x nanoparticles
  - ✓ Confirming the optical change depending on oxygen content

Materials & Methods

- **Materials**
  - ✓ Working electrode: P-type Si wafer (<100>, B-doped, 0.001-0.003 Ω cm)
  - ✓ Counter electrode: Pt sheet (10 mm × 40 mm × 0.5 mm)
  - ✓ Electrolyte: 10 M NH_4F aqueous solution

- **Sample preparation**
  - ✓ Anodization: Easy route to synthesize diverse metal oxide nanoparticles[2]
  - ✓ Applied voltage: DC 7.5, 10.0, and 12.5 V
  - ✓ Reaction time: 1 hr
  - ✓ Anodization temperature: 5 ℃ using a thermostat
  - ✓ Rinsing particles with DI water & filtering them under vacuum

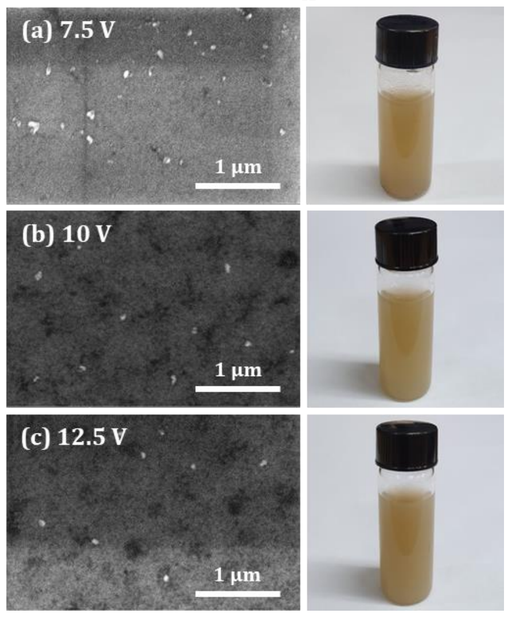


▲ Schematic view of anodization system

- **Sample characterization**
  - ✓ FESEM: Magellan400, FEI, USA
  - ✓ XPS: K-alpha, Thermo VG Scientific, USA → Al Kα radiation
  - ✓ UV-Vis: Lambda 1050, Perkin Elmer, USA

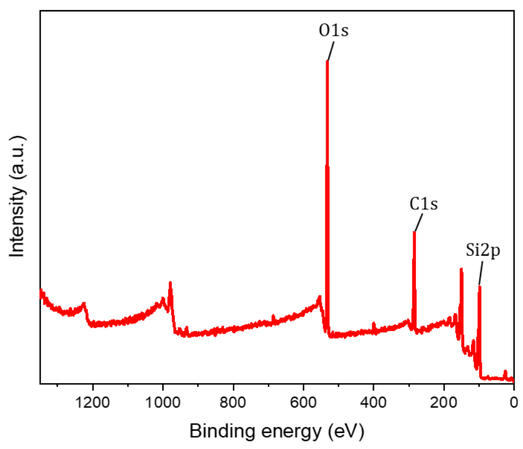
Results & Discussion

- **Synthesis of SiO_x nanoparticles**



▲ FESEM images and digital photographs of SiO_x nanoparticles synthesized at each anodization voltage: (a) 7.5, (b) 10.0, and (c) 12.5 V.

  - ✓ Average diameter: 62.9, 66.3, and 73.6 nm each for 7.5, 10.0, 12.5 V
  - ✓ Main elements: Si and O → SiO_x



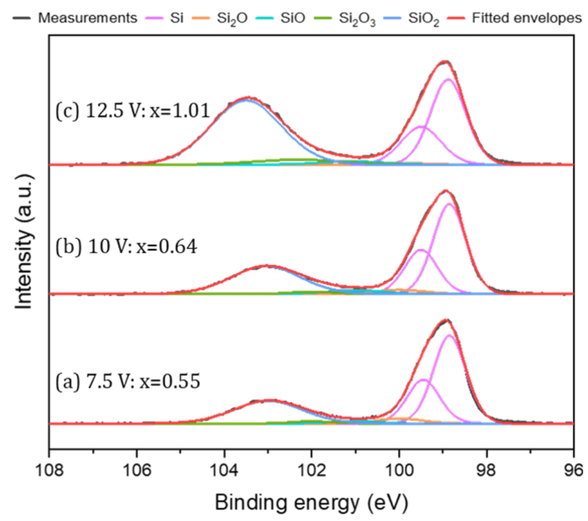
▲ XPS element survey of SiO_x nanoparticles synthesized at 7.5 V.

- **Oxygen content of SiO_x nanoparticles**
  - ✓ Five oxidation state of a Si atom: 0, +1, +2, +3, and +4
  - → Si-(Si_4), Si-(Si_3O), Si-(Si_2O_2), Si-(SiO_3), and Si-(O_4)
  - → Randomly combined each other to form amorphous phase
  - → Random bonding model for SiO_x
  - ✓ Different binding energy depending on each oxidation state
  - → Si-(Si_4) has two values of binding energy due to spin-orbital splitting[3]

▼ Oxidation number of Si and binding energy depending on oxidation state

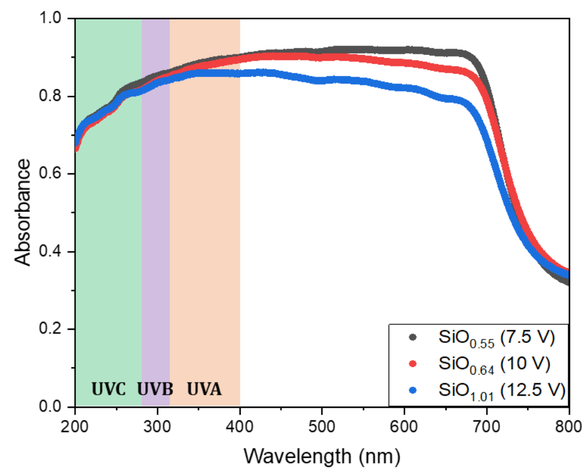
Oxidation number	Tetragonal structure	Chemical structure	Binding energy (eV)
0	Si-(Si_4)	Si	98.9/99.5
1	Si-(Si_3O)	Si_2O	100.0
2	Si-(Si_2O_2)	SiO	101.0
3	Si-(SiO_3)	Si_2O_3	102.0
4	Si-(O_4)	SiO_2	103.1

  - ✓ Oxygen content of SiO_x (i.e., x-value) can be calculated using the information of five oxidation state
  - → $x = \frac{0.0\times a+0.5\times b+1.0\times c+1.5\times d+2.0\times e}{a+b+c+d+e}$,
    a, b, c, d, and e: Peak area of each oxidation number (0 to 4) in XPS spectrum
  - ✓ X-value of SiO_x increases as applied voltage increases
  - → More O^{2-} ions react with Si which are produced during anodization
  - ✓ SiO_x nanoparticles with different oxygen content were obtained
  - → $SiO_{0.55}$, $SiO_{0.64}$, and $SiO_{1.01}$



▲ XPS Si 2p spectra of SiO_x nanoparticles synthesized at each anodization voltage and calculated x-values after peak deconvolution

- **UV absorption analysis**
  - ✓ Absorbance= $\log\frac{I_o}{I}$
  - → I_o: Initial intensity of wave
    I: Intensity after absorption
  - ✓ ~85% of UVA and UVB are absorbed by various SiO_x nanoparticles
  - → Slightly higher absorbance at lower oxygen content
  - → The number of oxygen vacancies increases as the x-value decreases, resulting in reduction in band gap
  - → The lower optical band gap, the greater UV absorption[4]



▲ UV/Vis photon absorbance of $SiO_{0.55}$, $SiO_{0.64}$, and $SiO_{1.01}$ nanoparticles

Conclusions

- **85% of UVA and UVB rays are absorbed by SiO_x nanoparticles prepared by anodization due to outstanding optical property**
- **SiO_x nanoparticles with lower oxygen content have higher UV absorption characteristic because of a lower optical band gap resulting from more oxygen vacancies**

Acknowledgement

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