ON THE KINETICS OF THE REMOVAL OF LIGANDS FROM FILMS OF COLLOIDAL NANOCRYSTALS BY PLASMAS

SANTOSH SHAW[1], TIAGO F. SILVA[2], PRATYASHA MOHAPATRA[1], DEYNY MENDIVELSO-PEREZ[3], XINCHUN TIAN[1], FABIAN NAAB[4], CLEBER L. RODRIGUES[2], EMILY A. SMITH[3], LUDOVICO CADEMARTIRI[1,5,6,]*

[1]*Department of Materials Science & Engineering, Iowa State University of Science and Technology, 2220 Hoover Hall, Ames, IA, 50011*
[2]*Instituto de Física da Universidade de São Paulo, Rua do Matão, trav. R 187, 05508-090 São Paulo, Brazil*
[3] *Department of Chemistry, Iowa State University of Science and Technology, Gilman Hall, Ames, IA, 50011*
[4] *Michigan Ion Beam Laboratory, University of Michigan, 2600 Draper Road, Ann Arbor, MI 48109, USA*
[5]*Department of Chemical & Biological Engineering, Iowa State University of Science and Technology, Sweeney Hall, Ames, IA, 50011*
[6]*Ames Laboratory, U.S. Department of Energy, Ames, IA, 50011*

[*] *Author to whom correspondence should be addressed: lcademar@iastate.edu*

SUPPORTING INFORMATION

MATERIALS AND METHODS

Particle synthesis

The synthesis and characterization of TOPO-capped ZrO_2 nanocrystals is the same as described in our earlier paper[1].

Characterization

X-ray Diffraction: Powder X-ray diffraction (XRD) was performed with Siemens D500 X-ray diffractometer at Materials Analysis and Research Laboratory (MARL) at Iowa State University. The diffraction pattern of plasma processed samples were collected from CNA spin-coated on silicon substrate for ZrO_2. XRD patterns were collected in 2ϑ range 20-60° by using 0.15DS, 0.05° steps, and 3s per step. For nanoparticle size analysis, diffraction pattern was collected in slow scan mode (0.03° steps and 20s integration) to improve peak-to-noise ratio. Accurate measurement of nanoparticles size using Scherrer equation was done following the procedure reported[2].

Raman Spectroscopy: Raman spectroscopy measurements were performed using an XploRa Plus confocal Raman upright microscope, equipped with a 532-nm laser excitation source (7 mW at the sample) and a Synapse EMCCD camera (Horiba Scientific/JY, France). A 50× air objective (Olympus, LMPlanFL) with a 0.9 numerical aperture was used to collect Raman signal under ambient laboratory conditions. Integrated peak areas of the C-H stretching region (2750 cm^{-1} to 3100 cm^{-1}) were an average of 3 measurements, each with a 60s acquisition time and 2 accumulations.

Scanning Electron Microscopy: Scanning electron microscopy was performed with FEI quanta 250 field-emission SEM at MARL at Iowa State University in secondary electrons mode at 10 keV with beam spot size of 3.

Scanning Transmission Electron Microscopy: High resolution TEM images were obtained using 2007 JEOL 2100 200kV STEM in TEM mode. This STEM is located at Microscopy and NanoImaging facility, Iowa State University. Samples for TEM analysis were prepared by evaporating drops of dilute nanocrystals dispersion at room temperature, on a carbon-coated copper grid. Thin film samples were prepared by scraping off flakes of CNAs from the substrate using a sharp blade, and then attaching them on a carbon-coated TEM grid.

Ion Beam Analysis: All ion beam analysis measurements were carried out at the Michigan Ion Beam Laboratory [3] at the University of Michigan with the 1.7 MV Tandetron accelerator.
The elemental analysis of the samples throughout the film depth was determined by combining Elastic Backscattering Spectrometry (EBS) and Elastic Recoil Detection (ERD) using a helium beam.
The EBS and ERD spectra were taken simultaneously at two different energies for each sample. A 3040-keV He^{++} beam was used for sensitivity to the oxygen signal through the EBS resonance at 3038.1 keV[4]. Similarly, a 4290-keV He^{++} beam was used for sensitivity to the carbon signal through the EBS resonance at 4265 keV[5].
The samples were mounted on a sample plate on the 5-axis goniometer of the 2 MV Tandem accelerator. The scattering angle of the EBS detector was 170° and of the ERD detector 30°. For each measurement the beam incident angle was 70°. The filter in front of the ERD detector was a 24 µm thick foil of Kapton ($C_{22}H_{10}O_5N_2$; density of 1.42 g/cm^3). The beam current on the samples during these measurements was ~20 nA with a beam spot of 1.5 mm by 1.5 mm.

The spectra evaluation followed a self-consistent approach enabled by MultiSIMNRA[6] that uses SIMNRA[7] code as engine to calculate the simulated spectra. The MultiSIMNRA code enables the combination of multiple spectra by the optimization of an objective function calculated for all spectra. The final depth profile results from the optimization algorithm as the model that best describes all experimental data. The information contained in one spectra act as boundary condition during the optimization of all the others.

All simulations used the SRIM stopping power[8] for energy loss calculations and SigmaCalc[9] scattering cross-sections of Helium in Oxygen and Carbon. For some reason that remain unclear, a better agreement to the experimental data was obtained using the scattering cross-section of Helium on Silicon provided in[10] rather than by SigmaCalc. Andersen screening function to Rutherford cross-sections[11] and the empirical model by Yang for the energy loss straggling calculations[12] were adopted. The geometrical straggling was accounted for in all simulations, and for the ERD simulations the multiple scattering was also calculated.

Simulation of Mass Transport in the Plasma Chamber. The simulation of the plasma chamber was carried out in a finite element software, COMSOL Multiphysics. The domain of the simulation was a 2-D adaptation of the Plasma chamber. The CNA sample and the mounting glass plate reside inside the plasma chamber, consistent with the experimental setup. The simulation was performed with pure oxygen as the feed gas at 500 mTorr pressure and room temperature conditions. The inlet velocity was obtained from the applied oxygen flowrates during experimentation. The surface of the CNA film was considered to be a source of carbon dioxide gas influx to the chamber. The flux rate was estimated using the maximum experimental carbon etch rate. A steady state coupled transport of species and fluid dynamics multi-physics model was implemented in COMSOL.

A combined diffusion convection equation, in the following form, is used for solving the transport of the species:

$$\nabla.(-D_i\nabla c_i) + \mathbf{u}.\nabla c_i = 0$$

where, D is the diffusivity, $\mathbf{u}$ is the velocity vector, c is the concentration and the subscript i denotes O_2 or CO_2 species. The velocity vector $\mathbf{u}$ in the chamber is modelled by solving the momentum balance and the continuity equations as follows

$$\rho\nabla.\mathbf{u} = \mathbf{0}$$

$$\rho(\mathbf{u}.\nabla)\mathbf{u} = \nabla.[-p\mathrm{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)]$$

where, ρ is the density, p is the hydrostatic pressure and μ is the viscosity of the fluid. The inlet boundary conditions were same as the inlet stream to the plasma chamber. Zero normal flux and no-slip conditions were implemented at the chamber walls. The simulation domain was extensively meshed using physics-controlled triangular mesh.

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