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AC-STEM and HRSEM Investigation of Silica Nanoparticle Film Structure

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As part of an ARPA-E SHIELD (Single-Pane Highly Insulating Efficient Lucid Designs) project, we have been developing silica nanoparticle films up to 1 mm thick for use as transparent insulating coatings with thermal conductivity of 0.02 $\pm$ 0.01 W/mK, comparable to superinsulating silica aerogels [1]. We deposit these films through aerosol impaction-driven assembly (AIDA) to form mesoporous silica [2]. Synthesis of particles occurs in a plasma-enhanced chemical vapor deposition (PECVD) reactor from the reaction of silane and air. The particles are then accelerated through a nozzle by a pressure drop and they impact onto a substrate translated below.

To understand the factors affecting these scattering sites, we deposited samples of various porosity to measure the impact of porosity on microstructure, pore size distribution, thermal conductivity, and transmissivity. Barrett-Joyner-Halenda (BJH) pore size and volume analysis of pores via BET gas adsorption revealed that rather different pore size distributions, with peaks between 15 and 35 nm, result from changing volume porosity. This work explores the change of structure and properties at various film porosities ranging from 74% to 91%, therefore significantly different densities from 1.1 to 0.3 g/cm^3. Transmission and haze modeling found mean scattering sites to be 30 to 40 nm in diameter and the primary cause of visible haze, reducing total transmission and degrading the appearance of the coating [3].

We have turned to electron microscopy to better understand the microstructure that leads to the low thermal conductivity and light scattering. TEM and SEM have been used to analyze silica nanoparticle film structure before to show neutron damage [4]. Aberration-corrected scanning transmission electron microscopy (AC-STEM) has been instrumental to understanding the nanostructure of the silica nanoparticle films, especially because the material is amorphous. Figure 1 SEM shows the microstructure of the films to be layered. The layering is another important part of the structure because in some cases the interface between layers appears to be more porous with larger pores that can lead to increased light scattering. Looser packing of the interface layers leads to a different refractive index and apparent Bragg reflector effects depending on layer thickness. Each layer is deposited once at a time and the AC-STEM HAADF images display roughly 100 nm layers of film collected directly on holey carbon. The STEM images illustrate the tight networking of nanoparticles that leads to the pore size distributions of thick films. Part of the reason for tight pore size distributions is from impaction of nanoparticles on the top layer of the film which likely redistributes particles near the surface of the film. Conventional TEM revealed the size of primary particles to be 5 $\pm$ 1 nm diameter spheroids that are highly connected shown in the inset of Figure 1. Through our work developing the PECVD process, the primary particle size was reduced from 20 to 5 nm, leading to tighter networking of nanoparticles. There is a scaled relationship between pore size distribution and porosity among depositions with the same particle synthesis conditions, but the pore structure can change dramatically with differences in pressure, flow rate, and power. SEM in Figure 2 revealed large aggregates of nanoparticles, which are a source of light scattering. These aggregates apparently form due to particle impaction conditions that lead to film stress and due to deposited agglomerates or flakes from the reactor wall [5].

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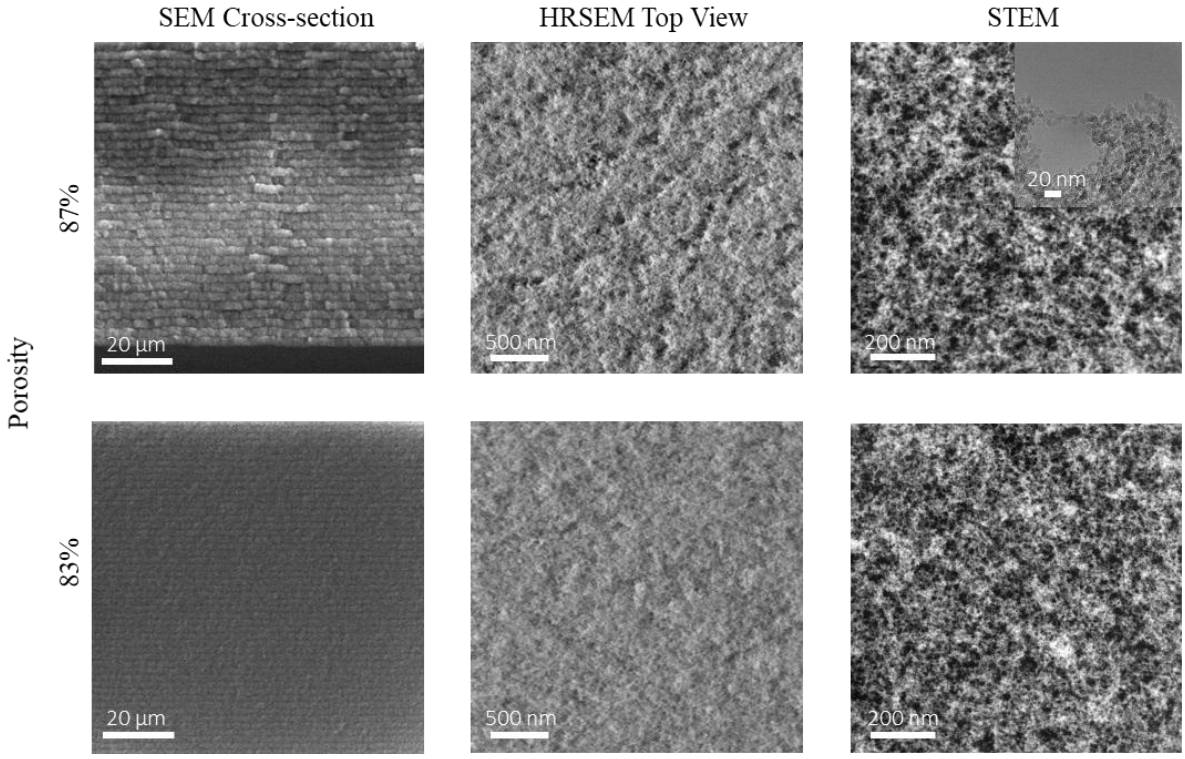

Figure 1. SEM cross-section and top view of films and STEM HAADF of one layer of nanoparticle film with porosities of 87% and 83%. The inset in the STEM image of 87% is a TEM image of the 87% sample to show the size of primary particles.

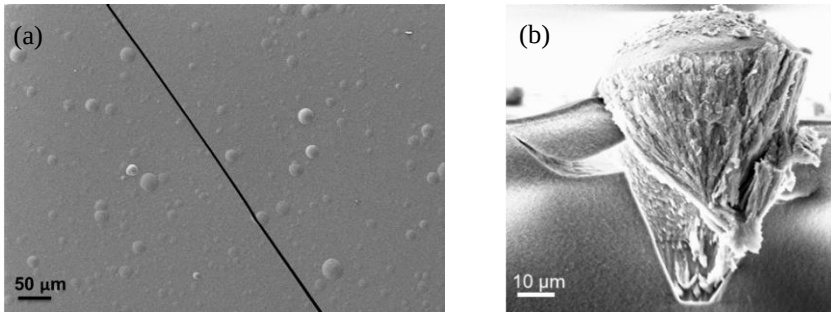

Figure 2. (a) SEM top view showing aggregates distributed on the surface and a crack running diagonally (b) SEM cross-section showing a silica nanoparticle aggregate.

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