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PHOTOACOUSTIC INVESTIGATION OF NANOPARTICLES ULTRA-THIN FILMS

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ABSTRACT

Ultrathin metal nanoparticles coatings are emerging as go-to materials in a variety of fields ranging from pathogens control to sensing. Accessing their mechanical properties is a crucial issue limiting their exploitation in real-life applications. The mechanical properties of metallic nanogranular thin films are unveiled exploiting ultrafast photoacoustic nanometrology in conjunction with bottom-up and top-down approaches based on more traditional techniques. Analytical homogenization methods are introduced, allowing to rationalize, in an easy-to-adopt scheme, both the films vibration frequencies and radiation damping. The latter yields important information on the granular films interfacial layer morphology. Building on the acquired knowledge a variety of applications are proposed, ranging from nano-fluid infiltration sensing to gas-phase separation and bendable electronics.

1. INTRODUCTION

Nanogranular materials are investigated for applications in fields ranging from transparent conductive electronics [1] to pathogens control [2-5]. As for the mechanical properties, work has been done on single and diluted nanoparticles (NPs) while a lack of informations remains for NPs deposited on a substrate and forming a thin film. Control on the NP composition, NP size, film thickness and uniformity, together with non-destructive probes for mechanical nanometrology, are needed in order to obtain mechanical information on such systems. The nanometrology of NPs thin film is here addressed both via bottom-up and top-down approaches. Ultimately, a virtual NPs film scaffold is obtained, allowing to engineer, beyond a trial and error approach, several device and applications schemes. Applications in the field of nano-fluid sensing, gas-phase separation and bendable electronics are discussed.

2. METHODS

NP Film Synthesis and Characterization. Ag NPs films were deposited at room temperature in medium vacuum conditions (base pressure 1×10^{-6} mbar) by supersonic cluster beam deposition (SCBD). The nominal film thickness and deposition rate were measured by a quartz microbalance, while film properties where obtained ex situ by AFM, XPS, Auger Spectroscopy and XRD. The size-distribution of the nanoparticles and their kinetic energies were retrieved respectively from high resolution high angle annular dark field−scanning transmission electron microscopy (HAADF-STEM) and gas-dynamics calculations.

Picosecond Acoustics. The Ag NPs films mechanical properties were investigated by means of pico-second photoacoustic, exploiting Asynchronous Optical Sampling technique.

Molecular Dynamics. All of the simulations were performed with the LAMMPS package. The velocity-Verlet algorithm is used to solve the equations of motion. As for the description of the Ag−Ag interactions, a 12−6 Lennard-Jones potential was used to simulate the NPs film growth whereas an embedded atom model potential (EAM) was adopted to estimate the film elastic constant.

3. DISCUSSION

The films are composed of juxtaposed Ag NP crystallites, average dimensions in the 6 nm range, and inter-NPs voids. The acoustic spectra are well accounted for in terms of continuum mechanics. Specifically, analytical homogenization methods allow to rationalize, in an easy-to-adopt scheme, both the films vibration frequencies and radiation damping. These results, quite surprising given the granular nature of the NP film, are particularly striking when one considers that the films are composed of only few layers of Ag NPs. The density, longitudinal sound velocity, and elastic stiffness have been measured for Ag NP films down to 15 nm thicknesses. The first two values are 80% and the latter 50% of the respective values for bulk polycrystalline Ag [6].

A virtual film model is proposed [7] merging high - resolution scanning transmission electron microscopy, supersonic cluster beam dynamics, and molecular dynamics simulations. The model is benchmarked against the figures obtained from the above-mentioned mechanical nano-metrology measurements and is readily extendable to metals other than Ag. The virtual model may be deployed to engineer, beyond a trial and error approach, a variety of devices, relevant in fields as Mesoscale Gas-Dynamics, Photoacoustic Sensing of Trapped Fluids and Transparent Conducting Materials (TCM).

Mesoscale Gas-Dynamics. The NPs film is inherently porous, and the virtual film scaffold has open porosity with an average-pore diameter of 5nm, see Figure 1, thus setting the gas transport across the film in the Knudesn regime. This fact, together with the possibility of spraying the NPs on virtually any surface, makes the film potentially appealing for distributed gas-dynamics applications. For instance, in the industrially relevant case of the ammonia synthesis process, the purge gas is composed of an H_2/N_2 mixture. The recovery of the two gas species is an important aspect, reducing both energy and environmental costs. For the specific case here addressed, the membrane selectivity is $\alpha_{H_2/N_2} \approx 3$, thus allowing the two species to be effectively separated [7].

Photoacoustic Sensing of Trapped Fluids. Accessing fluid infiltration in nanogranular coatings is an outstanding challenge, of relevance for applications ranging from nanomedicine to catalysis. A sensing platform, allowing quantifying the amount of fluid infiltrated in a nanogranular ultrathin coating, with thickness in the 10–40 nm range, is theoretically investigated by multiscale modeling. [8] The scheme relies on impulsive photoacoustic excitation of hypersonic mechanical breathing modes in engineered gas-phase-synthesized nano-granular metallic ultrathin films and time-resolved acousto optical read-out of the breathing modes frequency shift upon liquid infiltration, see Figure 2. A superior sensitivity, exceeding 26×10^3 cm^2/g, is predicted upon equivalent areal mass loading of a few ng/mm^2. The capability of the present scheme to discriminate among different infiltration patterns is discussed.

Transparent Conducting Materials. Based on the acquired knowledge, stemming from the mechanical nanometrology investiagtion, the multilayer structure AZO/ AgNPs/AZO, in which a 10 nm thick nanogranular Ag inter-layer (AgNPs) is sandwhiched between two 40 nm thick Aluminum-doped Zinc Oxide (AZO), is proposed. When compared to standard sputtered Ag film, the AZO/AgNPs/AZO system presents several important aspects for practical applications: a higher optical transparency and lower reflectance in the 500–1200 nm wavelength range, a higher electrical reliability and stability during sequential bending, a higher flexibility and capability in enduring external stresses, with much less structural damage[1].

4. CONCLUSIONS

Ultrathin metal nanoparticles coatings are emerging as materials bearing a great potential for applications in a variety of fields. Accessing their mechanical properties is a crucial issue limiting their exploitation in real-life applications. The mechanical properties of Ag NPs films are here investigated merging a top-down and bottom-up approach based on picosecond ultrasnoics, molecular dynamics and more traditional characterization techniques. Based on the knolwedge acquired on the system mechanics, several applications are discussed.

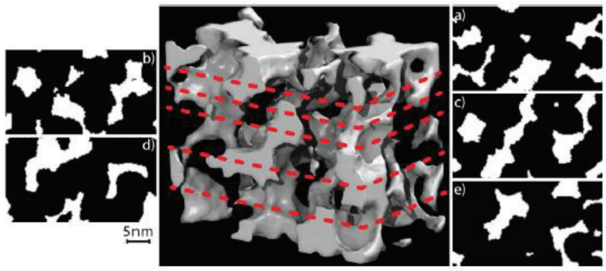

Figure 1. NPs film 3D voids scaffold (white), see Ref. [7].

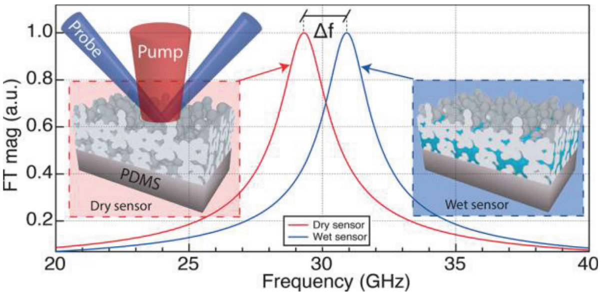

Figure 2. Photoacoustic sensing of trap fluids: principle of operation, see Ref. [8].

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