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Influence of sintering necks on the spectral behaviour of ITO clusters using the Discrete Dipole Approximation

Krzysztof Skorupski [a,*], Jens Hellmers [b], Wen Feng [b], Janusz Mroczka [a], Thomas Wriedt [b], Lutz Mädler [a]

[a] Wroclaw University of Technology, Chair of Electronic and Photonic Metrology, Boleslawa Prusa 53/55, 50-317 Wroclaw, Poland
[b] Foundation Institute of Materials Science (IWT), Department of Production Engineering, University of Bremen, Bremen, Germany

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ABSTRACT

In this paper we study the spectral behaviour of indium tin oxide (ITO) nanoparticle clusters using different sinter neck models for the connections between the primary particles. The investigations include light scattering calculations based on the Discrete Dipole Approximation (DDA). The corresponding clusters are generated using the Cluster–Cluster algorithm proposed by Filippov et al. Different sintering neck models led to significantly different spectral features. A spectral neck factor that reveals the thickness of the necks connecting the primary particles with a simple measurement method is introduced.

1. Introduction

Nano-particles of the same kind (material, size, shape) can show different properties depending on their spatial arrangement. Agglomerates of sintered nanoparticles are usually divided into two groups (see e.g. [1]): 'soft agglomerates' characterized by weak van der Waals forces holding the particles together and 'hard agglomerates' where the particles are bound chemically, leading to sintering necks and a different surface-to-volume ratio. Both types of agglomerates can lead to different behaviour for conductivity, appearance, rigidity, etc. – see e.g. Jiang et al. [2]. For designing material properties based on such geometry effects and their subsequent production, the ability to distinguish between soft and hard agglomerates is of great importance.

Here, we use light scattering simulations based on the Discrete Dipole Approximation (DDA) [3] to investigate the spectral behaviour of fractal clusters consisting of indium tin oxide (ITO) nanoparticles. ITO, while transparent in thin layers in the visible wavelength region, works as a metal-like mirror in the infra-red region. We chose this conducting oxide for a preliminary case-study to investigate possibilities for the development of an in situ, non-destructive measurement method to determine the thickness of the necks connecting the primary particles of clusters.

In this work we concentrate on optical effects caused by differently sized sintering necks in clusters of spherical ITO primary particles. Such connections were previously studied e.g. by Hellmers et al. [4] for two silver particles, or by Skorupski et al. [5] for black carbon (BC) aggregates. In this paper we are looking for characteristic spectral features which would allow us to derive a specific parameter to describe the connections between the primary particles of a cluster. Such a technique would be useful for on-line measurements in process control [6].

2. Refractive index of ITO

Indium tin oxide (ITO) is a conducting oxide that appears transparent in the visible wavelength area. We use the Drude model approach (see e.g. [7]) to calculate

* Corresponding author.
E-mail address: krzysztof.skorupski@pwr.edu.pl (K. Skorupski).

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the corresponding values for the real and the imaginary part of the refractive index. Here, the data published by Franzen [8] is the base for the calculations. Fig. 1 shows the permittivity, the refractive indices (n,k) and the reflectance of the bulk material [7]. The permittivity values of the bulk material also can be used to identify regions of plasmon resonances [9]. From Fig. 1 it is obvious that a spectral investigation of ITO has to be extended to near infrared wavelengths.

3. Fractal-like aggregates

The easiest way of creating aggregate models is to use equivalent-volume spherical particles. However, such a simplification might result in many light scattering simulation errors [10]. The morphological parameters of aggregates can be described by using the fractal geometry and the following equation [11]:

$$N_p = k_f \left(R_g / r_p\right)^{D_f}, \tag{1}$$

in which r_p is the particle radius, k_f is the fractal prefactor and D_f stands for the fractal dimension, which is the main parameter defining the overall shape of the structure – the larger its value the more compact is the aggregate. It varies from D_f=1 (e.g. a line) to D_f=3 (e.g. a cube) and generally is independent of the aggregate size. The fractal prefactor k_f is the parameter that is responsible for the equality sign in Eq. (1). Its value is dependent on the aggregate generation conditions. The radius of gyration R_g is defined as follows:

$$R_g^2 = \frac{1}{N_p} \sum_{i=1}^{N_p} (\vec{r}_i - \vec{r}_0)^2, \tag{2}$$

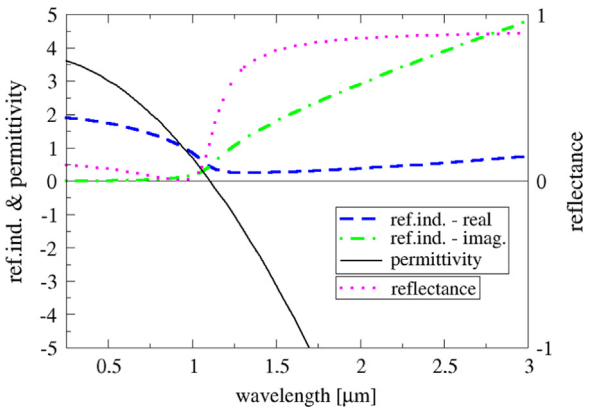

Fig. 1. Permittivity, refractive indices (n,k) and reflectance of bulk material ITO; data by Franzen [8].

where $\vec{r}$ is the position of the ith particle and $\vec{r}_0$ is the mass centre of the aggregate. Eq. (2) is a common approximation widely used in modeling and analysis of fractal-like aggregates [12–15]. It should be noted that there are also different equations, like e.g. by Filippov [16], or by Oh et al. [17], which take into account the radius of gyration of a single sphere. In this work we use Eq. (2) as it has proven to deliver sufficient results, especially as we use monodisperse spheres as primary particles only. For the creation of small aggregates, i.e. composed of N_p=5 primary particles, we used a PC (Particle–Cluster) algorithm and for larger structures we used a CC (Cluster–Cluster) algorithm, which provides more accurate models. Both techniques are based on the work by Filippov et al. [18]. Our implementation reduces the computational time and minimizes the position error that might occur between primary particles. The procedure is described in the work by Skorupski et al. [19]. To characterize fractal aggregates, D_f and k_f are the main parameters for the fractalness of the aggregate. They are independent of the size of the structure. N_p, r_p and R_g are varied as they define the number of primary particles, their radii and their mean distance from the aggregate center. We chose $D_f \approx 1.8$ and $k_f \approx 1.3$ for our work as these are typical values that lead to realistically shaped clusters [11], what is presented in Fig. 2.

To characterize the growing neck between the primary particles of a cluster we used a cylindrical model, which is presented in Fig. 3. It can be visualized as a cylinder with radius r_{con} positioned between the centres of two monodisperse particles with a radius r_p defined as

$$r_{con} = r_p \cdot Y_{con}, \tag{3}$$

Y_{con} stands for the unitless neck size parameter which varies from $Y_{con}=0$ (no connection) to $Y_{con}=1$ (full connection). Necks with $Y_{con}<0.4$ have an almost negligible volume which results in an insufficient number of volume elements (dipoles) for DDA calculations, see Fig. 3. In our work, we kept the total volume of the aggregate, V, constant and the relative volume error lower than $\delta V < 0.05\%$. Therefore, a reduction of the particle radius r_p compensated the growth of the neck Y_{con}. Note that the primary particles never change their position (their centre coordinates are fix), regardless of the neck size parameter Y_{con}. Such an approach models the early stages of the sintering phenomenon [20].

4. Light scattering simulations

In the next part of our study we made sure that the Discrete Dipole Approximation (DDA) [21] method is capable of simulating the light scattered by aggregates

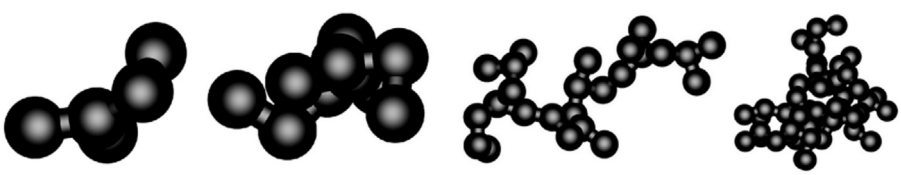

Fig. 2. ITO fractal-like aggregates composed of N_p=5, N_p=10, N_p=25 and N_p=50 primary particles. The neck size parameter is $Y_{con}=0.5$.