Nanoparticles

Effective medium approach for nanoparticles in colloidal and photonic crystals

Introduction

Photonic crystals are periodic structures of alternating high/low refractive index domains made of transparent materials. Those crystals can be non-transparent for a particular wavelength range due to multiple reflections and interference in the crystal. Theoretical calculations demonstrate [1] that for fcc (face cubic centred) crystals the ratio between the refractive indices of the different domains must be higher than 2.8 to form a photonic crystal with bandgap. These crystals are used as filters for electro-magnetic radiation, e.g. infra-red filters. The filter wavelength depends on the domain size and the refractive index difference between the domains. See [2] for a review of theoretical aspects of photonic crystals.

The present sample has a layer of silica spheres. The contrast of the refractive index of the glass spheres (1.46) and air (1) is too small to form a photonic crystal with band gaps. By contrast the silica spheres form a high ordered colloidal crystal. When colloidal crystals are infiltrated with a substance with high reflective index, and when the silica spheres are subsequently removed (etched with HF), an inverse opal is obtained with air spheres and a high refractive index material in the interstitial volume. An inverse opal can be applied as a photonic crystal with band gap. See [3] for material aspects of photonic crystals.

Actually the most common way for growing controlled-thickness-films of large diameter silica micro spheres is based on **a**ssisted and **i**sothermal **h**eating **e**vaporation **i**nduced **s**elf-**a**ssembly, AEISA [4] and IHEISA [5] respectively. In both methods a substrate is held vertically in an ethanol dispersion of silica micro spheres. A well-ordered colloidal crystal film deposits on a substrate at the air-liquid interface driven by convective and capillary forces. By contrast the periodic structures of spheres on this sample are produced by the Langmuir-Blodgett method. In order to control and optimize the production of such a colloidal crystal it is necessary to measure the diameter of the spheres, the number of planes of spheres, and the density of spheres in each plane.

Sample

layer: SiO_2-spheres, substrate: glass slide (BK7)

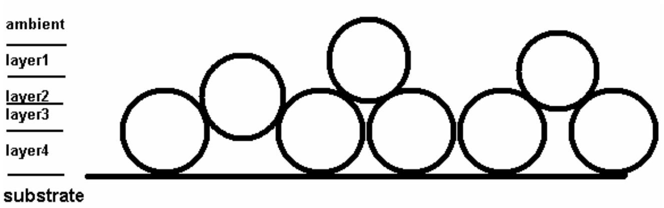

Fig.1: Schematic cut through sample and effective medium model of the sample by means of 4 layers

Instrumentation

Scanning Probe Ellipsometric Microscope (SPEM) including Imaging Ellipsometer EP³-SW (532 nm) with 20x-objective and scanning probe microscope (Ultra-Objective UO)

Task

Identification of the 3-dimensional distribution of spheres on the sample

Steps of evaluation

1. Automatic measurement of Delta/Psi in 2 zones as a function of the angle of incidence.
2. Fit with optical model in order to obtain the volume fraction of the SiO_2-spheres as a function of the layer thickness (fig.3). The volume fraction of layer 1 represents the density of spheres sitting on top of the dense filled bottom plane of spheres.
3. Scanning probe micrograph to measure the sphere diameter and to verify the density of spheres in the bottom plane and in the second plane.

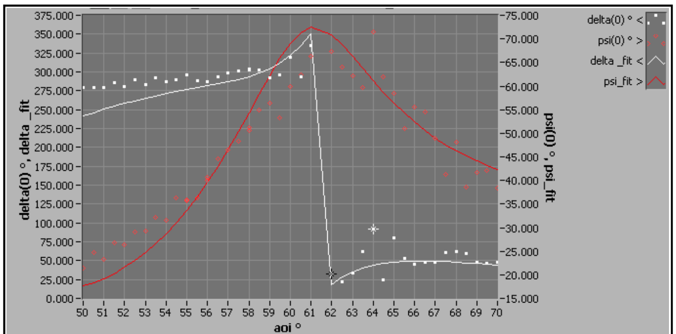

Fig.2: Screenshot from EP³View 2.0 Software: Delta/Psi angle of incidence spectra, 2-zone average at 532 nm wavelength, fit with 4-layer optical model gives results of tab.1 and fig.3

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Detail

Effective medium approach

Fitting the delta/psi spectra of fig.2 needs an optical model of the sample. The simplest model collects the spheres in one layer, which has a thickness d and a refractive index n. Since this layer is a mixture of spheres and air, n is expected to be between 1 (for air) and 1.46 for SiO_2. The theory of electrodynamics gives the dielectric constant of SiO_2-spheres in air $\varepsilon = \frac{2z+1}{1-z}$ with $z = f\frac{\varepsilon_{SiO2}-1}{\varepsilon_{SiO2}+2}$ where f means the volume fraction of the spheres in air, and the refractive index $n = \sqrt{\varepsilon}$. This particular mixture is assuming that the unit cell of volume includes a sphere of radius r and dielectric constant ε. This simple effective medium approach is called Lorentz model. If this approach is used to describe the layer, the volume fraction f is replacing the refractive index n as a free parameter to solve for. The spectrum (fig.2) is well fitted already in the one layer Lorentz model, where thickness d = 495 ± 5 nm and f = 0.45 ± 0.01 are statistical mean values for the layer result. A more precise model and a better fit of the spectra are obtained when the volume fraction f is decreasing stepwise from the maximum value 0.6 on the interface substrate-layer4 to zero at the interface layer1-air. A closely packed 2-dimensional lattice of spheres has f = 0.60 volume fraction. The more detailed model has 4 Lorentz layers with a priori constant volume fractions: 0.15, 0.3, 0.45, 0.6. The thicknesses of these 4 layers (see optical model parameters in tab.1) are evaluated by fitting on the spectra (fig.2). The sum of thicknesses of these 4 layers is almost the same as the thickness in the one layer model, but a vertical distribution of the volume fraction of spheres in the layer (fig.3) is additionally obtained in the 4 layer model.

Measurements

The volume fraction of the spheres (fig.3) is 0.6 for the lower 337 nm (layer4) of the mixed layer. This means that (337nm/460nm =) 73 % of the bottom plane of spheres is closely packed. This means that the spheres form a hexagonal 2-dimensional lattice, which is a promising prerequisite to form a colloidal crystal from SiO_2. But the lattice suffers from defects, where one finds randomly distributed outstanding spheres without contact to the substrate. In a macroscopic model these upper layers are represented by the upper layers 2 and 3 which have together approximately 160 nm thickness with volume fractions 0.30 and 0.45.

The scanning probe micrograph (fig.4) confirms the observation of a closely packed plane of spheres. But it cannot observe the number of planes layered on top of each other, because the needle (diameter 20 nm) of the cantilever cannot reach the substrate between the spheres (fig.5). By contrast the ellipsometer observes that the sum of the thicknesses of all layers together is approximately equal to the diameter of the spheres. Thus it is concluded that there is only one plane of spheres.

The diameter of the spheres is 460 nm according to the scanning profile (fig.4, 5). Thus the uppermost layer1 represents spheres sitting in a second plane on top of the closely packed bottom plane of spheres. The ellipsometer measures for layer1 44 nm statistical thickness (corresponding to 9.6 % volume of a closely packed layer) with ¼ of the volume fraction of the closely packed layer of spheres. In conclusion the ellipsometer observes (9.6 % / 4 =) 2.4 % of the sample area filled with spheres on the second plane. When spheres are directly counted in the scanning probe micrograph (fig.4). about 2 % of the sample area is observed to be filled with spheres in the second plane. In conclusion we have found agreement of ellipsometric and scanning probe measurement.

substrate (BK7 glass)		layer 1		layer 2		layer 3		layer 4	
n	k	f	d [nm]	f	d [nm]	f	d [nm]	f	d [nm]
1.5183	0	0.15	**44 ± 33**	0.30	**37 ± 40**	0.45	**91 ± 43**	0.60	**337 ± 27**

Tab.1: fit result (bold), other parameters are according to literature

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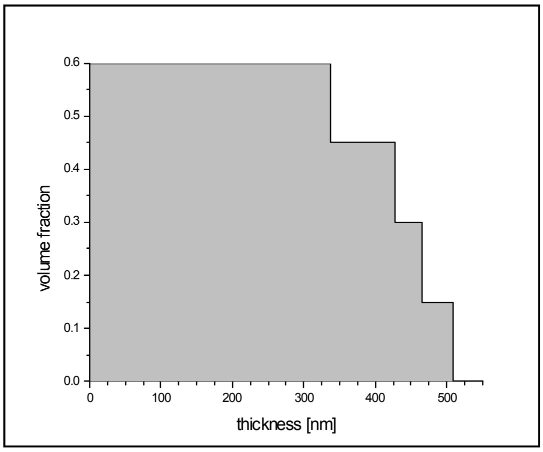

Fig.3: Volume fraction of SiO_2-spheres as a function of the layer thickness

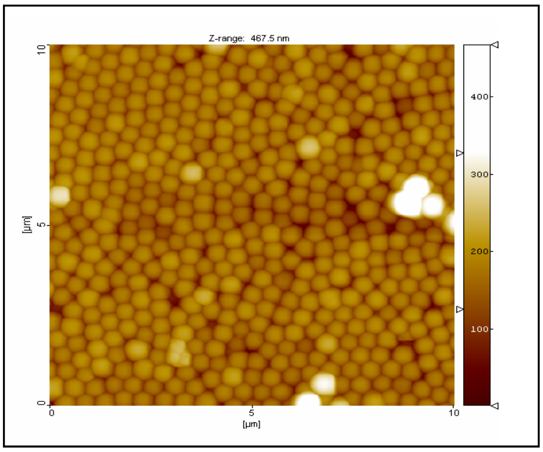

Fig.4: Scanning probe micrograph of the spheres, recorded in contact modus

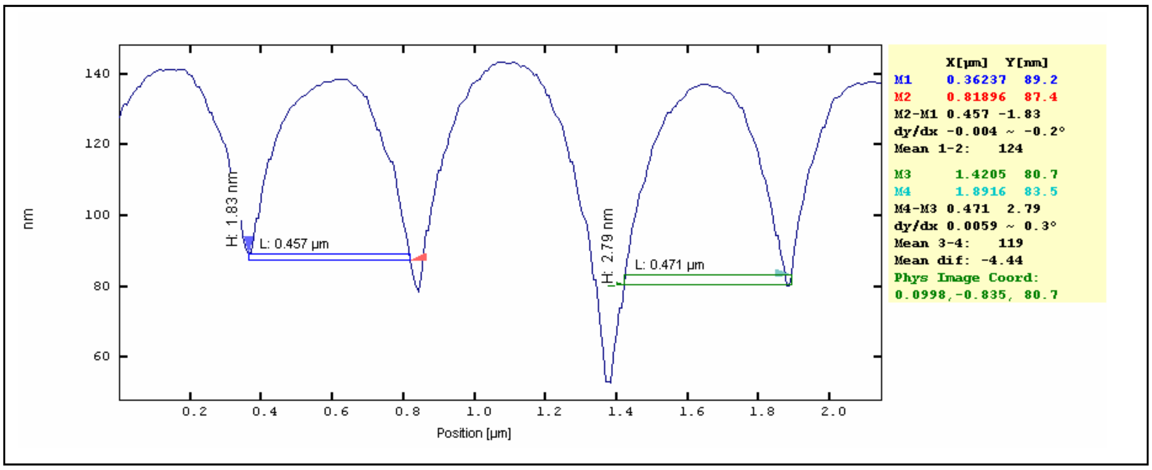

Fig.5: Profile of the top of the spheres cut through fig.4. The sphere diameter (464 nm) is obtained from this profile

Results

The diameter of the spheres 464 nm is measured by the scanning probe microscopy. The number of planes on top of each other is one according to the observation with the ellipsometer. 73 % of the plane is closely packed. Both, scanning probe microscope and ellipsometer observe defects in the plane and that there are about 2 % of the next plane on top are also

Conclusion

The imaging ellipsometer EP³ can evaluate the fundamental optical properties of a 2D-colloidal crystal. The ellipsometric observation is completed and verified by the scanning probe microscope (UO). The scanning probe ellipsometric microscope (SPEM) unifies both instruments in one. The SPEM is perfectly suitable to characterize photonic crystals and other nano-struc-tured surfaces.

Acknowledgement

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References

[1] John D. Joanopoulos, Roberdt D. Meade, Joshua N. Winn, Photonic Crystals, Molding the Flow of Light, Princeton University Press, 1995.

[2] J. D. Joannopoulos, Pierre R. Villeneuve and Shanhui Fan, Photonic crystals: putting a new twist on light, *Nature*, **386**, 143-149 (1997).

[3] Cefe López, Materials Aspects of Photonic Crystals, *Advanced Materials*, **15**, 1679-1704, (2003)

[4] S. M. Yang, H. Miguez and G. A. Ozin, J. *Adv. Funct. Mater*.,2002, **12**, 425

[5] S. Wong, V. Kitaev and G. A. Ozin, *J. Am. Chem. Soc.*, 2003, **125**, 15589

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