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L. LANDSTRÖM
D. BRODOCEANU
N. ARNOLD
K. PIGLMAYER
D. BÄUERLE✉

Photonic properties of silicon-coated colloidal monolayers

Institut für Angewandte Physik, Johannes-Kepler-Universität Linz, 4040 Linz, Austria

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ABSTRACT The spectral dependence of the optical transmission through hexagonal monolayers of silica (a-SiO_2) microspheres covered with different amounts of amorphous silicon (a-Si) is studied. The strong changes in the spectral transmissivity can be semi-quantitatively understood by the coupling of the incident electromagnetic field to photonic modes of the combined structure consisting of the hexagonal lattice of a-SiO_2 microspheres and a-Si.

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The enhancement of the electromagnetic field near single microspheres has been studied experimentally and theoretically in connection with laser cleaning, patterning, and modification of solid surfaces [1–3]. If the diameter d of microspheres is large in comparison to the wavelength λ of the incident light, the focusing properties of spheres can be described by a quasi-classical approximation of geometrical optics. If, however, the size of spheres becomes comparable to λ, the Mie theory has to be employed. Regular two-dimensional (2D) periodic lattices of microspheres can be formed over relatively large areas from colloidal solutions. Due to the focusing properties of microspheres, such colloidal monolayers can be employed as microlens arrays for single-step parallel laser processing [3–7]. There are, however, a number of other interesting applications. Microspheres in regular 2D or 3D lattices with lattice constants d of the order of λ behave like "atoms" in crystalline solids. Thus, such lattices show Bragg resonances at optical wavelengths. Similar to electrons or phonons in crystalline solids, such colloidal lattices show photonic band effects. As such lattices permit to manipulate electromagnetic waves at optical frequencies, they are also denoted as photonic crystals. Subsequently, we concentrate on 2D lattices of dielectric microspheres. The optical properties of such lattices have been studied in [8–11]. Recently, however, we have demonstrated that these optical properties can be significantly altered by metal coatings [12, 13].

In the present paper we report on monolayers of dielectric microspheres that are covered with different amounts of amorphous silicon (a-Si). The photonic properties of such "mixed" structures can be tuned via the size of spheres and/or the thickness of the deposited layer. Both of them modify the effective refractive index.

Figure 1 shows a scanning electron microscope (SEM) picture of a monolayer of amorphous quartz (a-SiO_2) microspheres on a thin a-SiO_2 platelet as support. The lattice is coated with a 125 nm thick a-Si film, which was deposited by standard electron-beam evaporation in a vacuum chamber. As with metal-coated monolayers discussed in [12, 13], the upper half of single spheres is silicon-coated while the lower half remains uncoated. The thickness of the coating at the top of spheres is about equal to that measured by a nearby quartz-crystal microbalance (QCM). In the interstices between three neighboring spheres, the coating is placed on the quartz support.

The optical transmission spectra shown in Fig. 2 for both coated and uncoated monolayers (ML) were recorded at normal incidence by means of an UV- to near-IR-spectrometer (CARY 500). The most pronounced features in the optical spectrum for uncoated ML of a-SiO_2 microspheres (dash-dotted curve) are the overall decrease in transmitted intensity towards shorter wavelengths and the dip at $\lambda \approx 1585$ nm. Besides of this pronounced dip, there are indications for other features at shorter wavelengths. For stochastic lattices fabricated by pulsed-laser deposition (PLD) [14] from a pellet of microspheres, the dip at 1585 nm vanishes. Thus, this feature is definitely related to the translational symmetry of the

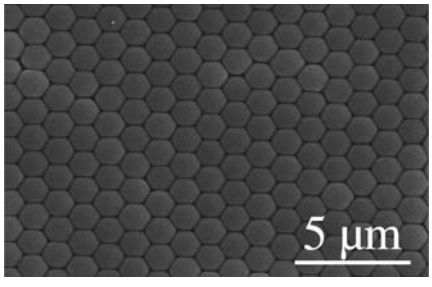

FIGURE 1 Scanning electron microscope (SEM) picture of a 2D lattice of quartz (a-SiO_2) microspheres of diameter $d = 1.42$ µm covered with a 125 nm layer of a-Si. The support is a 1.0 mm thick a-SiO_2 platelet

✉ Fax: +43-2468-9242, E-mail: dieter.baeuerle@jku.at

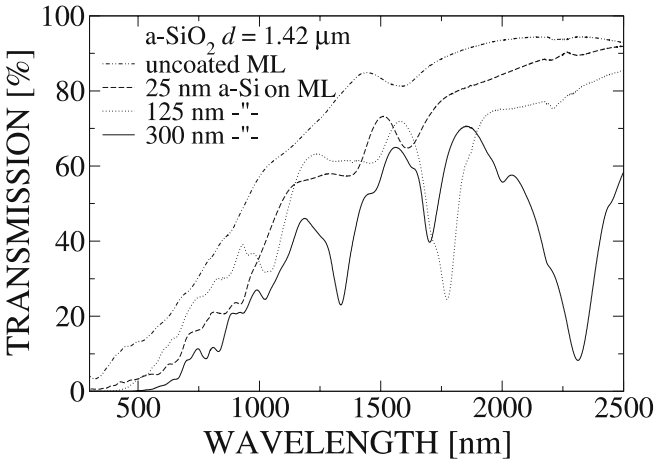

FIGURE 2 Transmission spectra measured at normal incidence for monolayers (ML) of a-SiO_2 microspheres ($d = 1.42\,\mu$m) covered with a-Si layers of different thicknesses. The *dash-dotted curve* refers to an uncoated lattice

2D lattice. If we cover the lattice with a layer of amorphous silicon, the dip at 1585 nm and the features at shorter wavelengths become more pronounced and simultaneously shift. This effect increases with the thickness of the a-Si layer which was varied between about 25 nm and 300 nm.

The present observations can be qualitatively explained along the following lines. The monolayer of silica spheres can be considered as a two-dimensional (2D) transmission diffraction grating. With such a grating, the zero order intensity transmission coefficient at normal incidence decreases with increasing parameter $kd \equiv 2\pi d/\lambda$. This is due to destructive interference of virtual sources from single primitive cells of the hexagonal lattice. This decrease in transmission may be further enhanced by parasite scattered radiation that is not collected by the spectrometer. These effects explain the overall decrease in transmitted intensity with decreasing wavelength. The dip in the transmitted intensity near 1585 nm is tentatively interpreted as a Rayleigh–Wood anomaly [15]. This anomaly is related to higher order diffracted waves. If such higher order diffracted waves propagate at a grazing angle to the surface of the grating, they may efficiently couple to surface modes. Thus, due to overall energy conservation, this coupling will cause an attenuation of the transmitted intensity. The dip at around $\lambda \approx 1585\,\text{nm} \gtrsim d$ is most probably related to such a mechanism.

The positions of Rayleigh–Wood anomalies can be estimated in the following way. For the 2D hexagonal monolayer and normal incidence, the first order diffracted waves have in-plane components with wavevectors $\boldsymbol{k}'_{\parallel} = \boldsymbol{G}$ where $\boldsymbol{G}$ is a reciprocal lattice vector. For first order diffracted waves $\boldsymbol{G} = \boldsymbol{b_1}, \boldsymbol{b_2}$ or some combinations of both. The diffracted wave can couple to photonic modes of the lattice with wavevector $\boldsymbol{k}$ if $k(\omega) \equiv n_{\text{eff}} k_0 = k'_{\parallel} = G = \frac{4\pi}{\sqrt{3}d}$. Here, n_{eff} is an effective refractive index. The last equality refers to the 2D hexagonal lattice, where the direction of the reciprocal lattice vectors $\boldsymbol{b_1}, \boldsymbol{b_2}$ is at 30° to the lines connecting the centers of adjacent spheres. Clearly, in a fully consistent approach, the values of n_{eff} should be taken from the dispersion curves $\omega(\boldsymbol{k})$ for the modes existing in a single monolayer of silica spheres. To calculate these curves is a non-trivial problem. The modes that must be considered propagate within the 2D lattice (x, y-plane) and they may be evanescent in z-direction. Thus, solutions of the full 3D vectorial Maxwell equations would be required. Numerical calculations of this kind were performed in [9] for polystyrene (PS) spheres with a refraction index of $n\,(\text{PS}) = 1.6$. They give reasonable agreement with our spectra for monolayers of uncoated PS spheres.

Our goal in this letter is, however, to study the behavior of colloidal monolayers covered with different amounts of a-Si. For this reason we adopt an extremely simplified description of the photonic modes. It is well known, that the contrast of bare artificial opal (SiO_2 spheres with air interstices) is not high enough to result in a true optical band gap [16]. As the modes that are important in our analysis propagate within the plane of the hexagonal lattice that consists of both silica microspheres and air gaps, we employ the crude "effective medium" estimation: $n_{\text{eff}} = nf + 1(1 - f)$ where n is the refractive index of the silica spheres and f their volume fraction in the slab of thickness d. For a single hexagonal monolayer we find $f = \pi/3\sqrt{3} = 0.61$. With $n\,(\text{SiO}_2) = 1.42$ this yields $n_{\text{eff}} \approx 1.25$. This value is in reasonable agreement with the value $n_{\text{eff}} = \frac{2\lambda}{\sqrt{3}d} = 1.29$ which we find from the position of the dip at $\lambda = 1585$ nm in the dash-dotted curve in Fig. 2 with $d = 1.42\,\mu$m. This description permits also a qualitative understanding of the spectra measured for different amounts of a-Si. Depending on the preparation technique, significant absorption of a-Si starts at around $\lambda \approx 1.05\,\mu$m to $1.3\,\mu$m [17]. The refractive index of a-Si depends on wavelength and also the preparation technique and varies within the range $3 < n\,(a\text{-Si}) < 5$. Therefore, the deposition of a-Si onto colloidal a-SiO_2 monolayers with interstices results in a higher refractive index contrast. The structure starts to resemble a 2D inverted artificial opal, which exhibits true band gaps and other non-trivial optical properties [18]. Thus, with increasing thickness of sputtered a-Si, and in particular the build-up of the material within the interstices, one expects an appreciable increase in the effective refractive index, and a much more pronounced structure of the photonic modes. This is in qualitative agreement with the red shift of the dips and their intensification observed in the spectra in Fig. 2. A detailed theoretical analysis of the dispersion relations for the optical modes within such a composite structure is far beyond the scope of the present communication.

In summary we emphasize that composite materials consisting of regular lattices of self-assembled colloidal microspheres and other materials permit simple fabrication of non-trivial 2D photonic structures with variable optical properties.

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