Highly dispersive micropatterns in ion-exchanged glass formed by ion irradiation through a mask of colloidal particles

We have fabricated refractive index gratings with hexagonal symmetry in Na\(^{+}\)\(\rightarrow\) Ag\(^{+}\) ion-exchanged borosilicate glass by ion irradiation through a mask of self-organised silica colloidal particles. The index increase in the irradiated regions of the glass is caused by the formation of silver nanocrystals under the influence of the ion beam. Light scattering measurements show diffraction rings and peaks belonging to hexagonal symmetry with a lattice constant approximately equal to the diameter of the particles in the colloidal mask.
The optical constants of composite materials formed by metal nanocrystals in an insulating background material are at the bottom of various interesting optical properties of such materials both in the linear (Kreibig, 1974) and nonlinear regime (Flytzanis et al., 1991). As for the linear optical properties, mainly the surface plasmon resonance absorption of such composites has been studied (Kawabata and Kubo, 1966; Tiggensbömker et al., 1992; Hövel et al., 1993). Paired with this absorption is a considerable variation of the real part of the index of refraction (Kreibig, 1970, see chapter 8 of this thesis). Silver nanocrystals in oxide glass have their plasmon resonance absorption in the violet around 420 nm. The corresponding variation in the real part of the index of refraction of such composites extends from the ultraviolet to the green.

The index of refraction of a glass containing silver ions can thus be changed by nucleating silver nanocrystals. In contrast to many other ions, silver can be introduced into oxide glasses containing network modifiers such as Na⁺ or K⁺ a posteriori via ion exchange, which allows for the incorporation of silver ion concentrations of several atomic percent. Silver nanocrystals can be formed by ion irradiation of the ion-exchanged glass (Arnold and Borders, 1977; Peters et al., 2000; Valentin et al., 2001, see also chapter 7). This formation process, in contrast to anneals in controlled atmosphere, opens the possibility to nucleate silver nanocrystals in selected regions of a sample only, and thereby change the index of refraction. A regular pattern of index variations can find application as a diffraction grating, waveguide multiplexer or photonic crystal. In this chapter we explore the formation of such regular refractive index variations making use of colloidal silica particles deposited on the ion-exchanged glass as an implantation mask. Colloidal particles self-organise on a flat substrate when the solvent evaporates (Denkov et al., 1992), forming a hexagonal array. Only in the spaces between the particles, formation of silver nanocrystals occurs when the sample is irradiated with an ion beam. The outcome is a highly dispersive hexagonal pattern written directly into the glass substrate.

9.1 Sample preparation and characterisation techniques

Borosilicate glass was ion-exchanged for 5 min at 320 °C in a 8.3 mol% AgNO₃/91.7 mol% NaNO₃ melt. Such an ion exchange gives rise to a surface layer in the glass with a graded Ag⁺ concentration up to a depth of around 1 μm. The silver concentration at the surface amounts to 7.5 at.%, as measured by Rutherford Backscattering Spectrometry. Colloidal silica particles of 1.66 μm diameter were prepared from seeds grown by the usual ammonia-catalyzed Stöber synthesis (Stöber et al., 1968) using a continuous growth set-up as described by Giesche (1994). They were dissolved in ethanol and deposited onto the ion-exchanged glass. The silica particles ordered into a two dimensional hexagonal array during the evaporation of the solvent (Denkov et al., 1992). They served as a mask for ion irradiation of the ion-exchanged glass.
FIGURE 9.1: Real and imaginary parts of the index of refraction of Ag ion-exchanged borosilicate glass before and after ion irradiation. The imaginary part of the glass index of refraction before irradiation does not exceed $2 \cdot 10^{-5}$ over the spectral range plotted and is not visible on the scale of the graph. The peaks in both real and imaginary part of the index of the glass after irradiation are caused by the surface plasmon resonance of small silver particles formed in the irradiated layer. The data was obtained from reflection and transmission measurements of samples prepared without a colloidal mask.

The glass with its mask of colloidal particles was cooled to 77 K and irradiated with Xe ions at an energy of 1 MeV to a fluence of $5 \cdot 10^{15}$ cm$^{-2}$. The projected range of the Xe ions in silica is around 450 nm, considerably less than the diameter of the mask particles. During irradiation with heavy ions, silver nanocrystals are formed in the glass (Peters et al., 2000, chapter 7) in a layer determined by the range of the implanted ions. This layer of glass/silver nanocrystal composite has an elevated index of refraction in the blue and green region of the visible spectrum (see chapter 8). After irradiation, the colloidal particles were removed from the surface of the glass.

The index of refraction of the composite layer was estimated by reflection and transmission measurements according to the method described in chapter 8 of this thesis. The samples used for this purpose were prepared under identical conditions, but had been ion-irradiated without mask. Figure 9.1 shows the index of refraction of the planar ion-exchanged and ion-implanted layer estimated from reflection and transmission measurements. The measurements are compared to the index of refraction of the unirradiated glass. The strong features in both the real and imaginary parts of the index of refraction with peaks at 442 nm and 430 nm, respectively, are caused by the
FIGURE 9.2: Reflection image of a region of the sample ion-irradiated through a colloidal mask, taken with a laser scanning confocal microscope at a wavelength of 488 nm, after the colloidal particles were removed. Light regions correspond to areas that reflect the light more strongly than dark regions. A hexagonal pattern of circular regions of low reflectivity is seen. This pattern is attributed to the masking effect of a hexagonal array of colloidal spheres with 1.66 μm diameter during ion irradiation. The inset shows a magnified image of a hexagonally ordered domain.
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The surface plasmon resonance of silver nanocrystals in glass (Kreibig, 1974). The average diameter of the silver nanocrystals is 2 nm (estimated from a fit of Mie theory (Mie, 1908) to the absorbance of the irradiated layer), with interparticle distances of the order of 10 nm. Both these values are very much smaller than the openings in the colloidal mask and than the wavelength of visible light. The glass/Ag nanocrystal composite in the irradiated regions of the masked sample is therefore as homogeneous as the one in the reference sample. This means that the optical constants of the irradiated regions of the masked sample are comparable to the ones determined for the reference sample.

The samples that had been irradiated through a mask of colloidal particles were analysed in a confocal laser scanning microscope in reflection mode at a wavelength of 488 nm after removal of the colloidal particles. We used a 100× objective lens with a numerical aperture of 1.4. Light scattering experiments were performed with a He-Cd laser operating at 442 nm in transmission geometry. The footprint of the laser on the sample was around 300 µm. The light scattered by the sample was projected onto a screen and imaged using a CCD camera.

9.2 Optical microscopy and light scattering

Figure 9.2 shows a laser scanning microscope image of the irradiated sample after removal of the colloidal mask. The image was taken in reflection mode at a wavelength of 488 nm. The light regions in the image correspond to areas that reflect light more strongly than the dark regions. The image consists of dark circular regions forming a polycrystalline hexagonal pattern in a light background. It is evident that this image reproduces the “shadow” of the colloidal mask, with the dark circles marking the positions held by the silica particles during the ion irradiation. The high reflectivity of the area where the glass/Ag nanocrystal composite has formed ($R = 0.16$) is a signature of the elevated index of refraction of these regions compared to the base glass ($R = 0.05$, see figure 9.1). The period of the hexagonal array measured in crystalline domains is $1.68 \pm 0.02 \mu m$, in close correspondence to the diameter of the silica particles used as the mask.

Light scattering experiments were performed to further study the structure of the sample. In this type of experiments, the reciprocal lattice of the scattering array is observed directly. A hexagonal array of scatterers also has hexagonal symmetry in reciprocal space. In figure 9.3 we show an image of the scattering pattern in transmission using 442 nm radiation on the same sample as depicted in figure 9.2. The polycrystalline configuration leads to the appearance of diffraction rings. Two rings, a strong inner and a weak outer ring (the latter not shown in figure 9.3), can be discerned. With the modulus of the scattering vector $k_{sc}$ evaluated as

$$k_{sc} = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}, \quad (9.1)$$

with $\lambda$ the wavelength in vacuum of the scattered light and $\theta$ the scattering angle, the
FIGURE 9.3: Diffraction image of an ion-exchanged borosilicate glass irradiated through a mask of colloidal spheres. On top of a diffuse ring, bright spots are observed that indicate the hexagonal symmetry of the arrangement of the scatterers. Part (b) shows the same data, overlayed by two hexagons, corresponding to diffraction from two differently oriented domains. The modulus of the scattering vectors associated with this pattern is approximately $3.9 \cdot 10^6 \text{m}^{-1}$, which corresponds to a lattice constant of 1.6 $\mu\text{m}$.
radii of the two rings correspond to scattering vectors of lengths $3.9 \pm 0.2 \cdot 10^6 \text{m}^{-1}$ and $7.0 \pm 0.3 \cdot 10^6 \text{m}^{-1}$. The ratio of these two values is $1/\sqrt{3}$ within our measurement error, which is to be expected for hexagonal symmetry. The values correspond to a lattice constant of $1.6 \pm 0.1 \mu\text{m}$. Identical values for the scattering vectors are obtained when light of different wavelengths in the blue and green is used. The scattering efficiency decreases, however, for longer wavelengths, in correspondence with the decrease of the index contrast (see figure 9.1). For $633\text{ nm}$ light, the scattered intensity was below the sensitivity of our measurement. Note that equation 9.1 describes scattering in vacuum and not in glass. It is valid in our case where the ratio between glass thickness and observation distance is small.

At several places on the sample the extent of the hexagonal domains is of the order of the footprint of the laser. There the light is scattered mainly from only one or two domains. The bright diffraction spots on the diffuse ring in figure 9.3 correspond to diffraction from such an area. These spots lie on the corners of hexagons, as is seen more clearly in figure 9.3 (b). It shows the same data as figure 9.3 (a), now overlaid with two hexagons connecting two sets of diffraction spots. This correlation is further evidence that diffraction takes place from hexagonally ordered scatterers.

From the width of the diffraction ring we can estimate the average size of the crystalline domains. At small angles (the ring in figure 9.3 corresponds to a scattering angle of $17^\circ$), the ratio between width and radius of the diffraction ring is approximately equal to the ratio between lattice constant and average domain diameter. This relation yields an average domain size of $17 \mu\text{m}$. This value is in good agreement with the average domain size observed in figure 9.2.

Measurements with an atomic force microscope in contact mode reveal that the irradiation with Xe ions changes the morphology of the surface: irradiated regions are elevated by $30 - 40 \text{nm}$ above the unirradiated areas. However, considering the aforementioned wavelength dependence of the scattering efficiency, this physical grating superposed on the index grating is not the principal mechanism causing the diffraction we observe. The wavelength dependence of the scattering efficiency of such a physical grating is considerably weaker than the one observed.

In the present experiment, the size of the colloidal particles used as the irradiation mask has been chosen such that the structures fabricated in the glass are clearly visible in an optical microscope. However, the technique described here is not limited to this size range. Smaller colloidal silica particles are even easier to fabricate than large ones and self-organise in the same fashion. The lower limit for the period of the grating is the range of the ions used to form silver nanocrystals in the glass. For the conditions used in our experiments, colloidal particles with a diameter of $600 \text{nm}$ are still sufficient to stop $1\text{ MeV}$ Xe ions whose range is around $450\text{nm}$ in silica. Two possibilities seem viable to further reduce the period of the structure written into the glass: a reduction of the ion energy used for the irradiation would alleviate the requirements on mask thickness and also produce shallower gratings; the use of different mask materials with higher stopping for Xe ions, such as Ag or Au (Graf and van Blaaderen, 2001), or of anisotropically shaped particles (which have to be
made to stand upright) will also lead to a shorter period, at unchanged properties of the glass/Ag nanocrystal layer. Let us also note that techniques have been developed to fabricate two-dimensional single-crystalline domains of colloidal particles on the centimeter scale. Using such domains of a size greater than the dimensions of the incoming light beam allows the diffracted intensity to be localised in the diffraction spots rather than a diffraction ring. Finally, colloidal particles can be deposited in arrays of other symmetries than hexagonal with the help of optical tweezers or a templated substrate (van Blaaderen et al., 2001). In this way a variety of diffraction symmetries become available.

9.3 Summary

In summary, we have fabricated hexagonally ordered arrays of scatterers in ion-exchanged glass by ion irradiation through a hexagonal mask of self-organised colloidal silica particles. The contrast of the refractive index between ion-irradiated and unirradiated regions is caused by the formation of silver nanocrystals under the influence of the ion beam. In light scattering experiments we observed diffraction patterns corresponding to hexagonal symmetry with a period of 1.6 \( \mu \text{m} \), which correlates well with the diameter of the silica particles used as implantation mask.