Gold-Ruby Glass in a New Light: On the Microstructuring of Optical Glasses with Synchrotron Radiation

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Abstract

We describe the microstructuring of gold-ruby glasses with synchrotron radiation. Plasmonic or luminescent microstructures with a lateral width of minimum 5 μm can be written directly into the glasses by implementing X-ray lithography. The technique involves two steps: First, gold containing glass samples are irradiated with synchrotron X-rays through a microstructured mask. And second, subsequent annealing at minimum 500°C induces the growth of gold nanoparticles. The patterned sites are ruby coloured due to the gold surface plasmon resonance of gold nanoparticles. Furthermore we investigated the photoluminescence of the microstructured glass. After synchrotron irradiation a red photoluminescence is observed under UV light excitation. Subsequent annealing for a few minutes at 300°C induces the quenching of the red luminescence. If the irradiated sample is annealed for 5 minutes at a higher temperature of 500°C a bright green light emission is detected. The green photoluminescence decreases after further annealing and finally vanishes. We assume that
the origin of the luminescence are silicate hole centres. The technique of generating gold particles with synchrotron X-ray lithography has potential to produce micro-optical devices like optical storage units, photonic crystals, gratings or sensors.

Introduction

Gold-ruby glass has been a fascinating material for centuries. Although few examples were manufactured during the time of the Roman Empire, the documented story of these glasses starts in 1689 with the German pharmacist and alchemist Johannes Kunckel (1). The eponymous ruby colour is caused by excitation of a collective oscillation of valence electrons in gold nanoparticles, called surface plasmon resonance. The wavelength of the plasmon resonance depends on the size, shape, topology and the dielectric environment of the metal clusters (2). An outstanding property of surface plasmons is the possibility to guide light in subwavelength metallic structures. Hence surface plasmon-based photonics, or "plasmonics", is thought to be an upcoming key technology for solving the dilemma of merging microscopic photonics and nanoscopic electronics in optoelectronic circuits (3). In addition to the surface plasmon resonance the photoluminescence of gold clusters is in the focus of modern research. Even though investigations had shown that gold nanoparticles emit light with extremely low quantum yields, Dickson et al. has recently reported on a size-dependent luminescence in the visible with remarkably high quantum yields of very small dendrimer encapsulated gold clusters (4). Another hot topic is the question whether and under which circumstances gold particles quench or enhance the luminescence of vicinal molecules (5). For further investigations and possible applications like the usage as sensor materials, optical storage media or optoelectronic devices the synthesis of stable, nearly monodisperse clusters of different diameters is indispensable. At this point the old gold-ruby glass comes into play again. Gold particles are long-time stable in glassy matrices and can be investigated easily due to the transparency of glass in the visible and near UV. We could show that different diameters of gold nanoparticles with narrow size distributions are accessible when gold doped soda-lime-silicate glasses are activated by synchrotron radiation and subsequently annealed (6).

Due to the superb properties of synchrotron X-rays like the short wavelength, high brilliance, high stability, and low divergence, it is ideally suited for lithography. Especially thick

samples can be patterned successfully. In this paper, we report for the first time on the microstructuring of gold-ruby glasses with synchrotron X-ray lithography. Furthermore absorption and luminescence properties of the microstructures induced by synchrotron light and subsequent annealing are discussed.

Experimental

Glasses composed of 70 $SiO_2 \cdot$ 20 $Na_2O \cdot$ 10 CaO (values in mol%) were doped with 0.01 mol% Au(III). Reagent grade SiO_2, Na_2CO_3, $CaCO_3$ and $AuCl_3 \cdot 2H_2O$ were used as starting materials. Approximately 35 g batches were mixed and melted at 1450 °C for 100 min in an electric furnace. The glass melt was then slowly cooled down to room temperature, cut to sizes of 10 x 10 mm^2 and polished to a thickness of 1000 ± 5 µm.

Selected samples were irradiated ("activated") on an area of approximately 8 x 8 mm^2 with synchrotron radiation from the Berlin electron storage ring BESSY. The irradiation dose was 40 J cm^{-2}. X-ray lithography was carried out under clean room conditions with the X-ray scanner DEX02 (Jenoptik MT GmbH) and a gold test mask with different micrometer structures. Thermal treatments were realised by putting the glasses into a platinum crucible and annealing it in a muffle furnace. UV/Vis absorption spectra were acquired with an ATI Unicam UV 4-200 UV/VIS spectrometer equipped with a deuterium/tungsten light source. Uncorrected luminescence spectra were recorded at room temperature with an Aminco Bowman Series 2 Luminescence Spectrometer equipped with a xenon light source for excitation and a KV 370 long pass filter (Schott) to suppress the excitation light in the fluorescence mode.

Results and discussion

Nonthermally activated growth of gold nanoparticles
To yield transparent, solid glasses, the component materials silicon dioxide, sodium and calcium carbonate are doped with 0.01 mol% gold(III) chloride and subsequently the mixture is melted at 1450°C for 100 minutes and cooled down. Previous investigations with XANES and Mößbauer spectroscopy have shown that gold is mainly in cationic form before either annealing or activation (6,7). For the nucleation and growth of the colouring gold colloids a reduction of gold ions to elemental gold is necessary. This can be realised by a longsome thermal treatment (8) or by activation of glasses with high energy irradiation like synchrotron light. A great advantage of the activation process is the separation of nucleation and growth of gold particles. Irradiation with synchrotron X-rays induces defect centres in the glass framework. Due to the breaking of silicon-oxygen-bonds electrons and holes are created. The growth of gold nanoparticles is initiated by subsequent annealing. While

gold ions, small clusters and nanoparticles are stable at room temperature in the glassy matrix, they become mobile at higher temperatures around the so called glass transition temperature T_g (for soda-lime-silicate glass $T_g \approx 525°C$) and can diffuse to form larger particles. The size of gold colloids and accordingly the surface plasmon resonance can be tuned by choosing the temperature and the time of the annealing process.

Microstructuring with synchrotron x-ray lithography
High aspect ratio microscopic devices like micro gears, micro optical benches or micro biochips, e.g., can be made with X-ray lithography today. Highly collimated synchrotron X-rays can penetrate with little diffraction or scattering into hundreds of microns of a photo resist. Due to the short wavelength used 3-dimensional structures with micrometer or sub-micrometer resolution in the lateral geometry, but with structural heights up to millimetres become accessible.

After the successful synthesis of gold clusters in glasses with hard Synchrotron X-rays patterning of the samples by X-ray lithography is self-evident. For the lithographic irradiation of gold containing glasses the entire spectrum provided by a dipole magnet of the synchrotron ring BESSY is used. Pre-examinations have shown that nucleation and growth of gold clusters do not depend on energy but only on intensity of synchrotron X-rays. For lithography we have used a 4 inch X-ray gold mask with test structures in the micrometer range made for the LIGA process (LIGA is the German acronym for *Lithographie* (lithography), *Galvanik* (galvanic) and *Abformung* (molding)). The production of the mask includes the following steps: First a negative resist (SU-8) is aligned on a graphite membrane and patterned by using an optical mask and a UV light source. The non-irradiated resist is then dissolved in an appropriate development immersion. Subsequently a 20 - 30 µm thick gold layer is electrodeposited on the site of the graphite membrane not covered by the photo resist. For X-ray lithography of gold-ruby glasses samples are aligned on a 4 inch boro float glass wafer and positioned in front of the X-ray mask in the exposure chamber. To adjust the irradiation dose reproducibly and to define the area of activation a
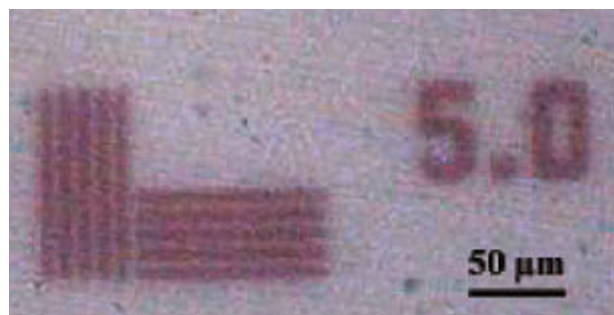

Figure 1
Light-microscopy image taken of structures in a gold-ruby glass, written with synchrotron X-ray lithography, and annealed for 30 minutes at 550°C. The width of lines and spaces is 5.0 µm

dipole X-ray scanner is used. The irradiation dose is defined by the number of scans in consideration of the beam current. This way we could write structures in the glass samples with a lateral width of minimum 5 μm (figure 1). Because the entire thickness of the glass was irradiated aspect ratios of more than 100 were achieved. The obtained resolution is also the limit of the used X-ray mask. With high resolution X-ray masks structures in the sub-micrometer range should be achievable.

Writing, reading and deleting

As already mentioned X-rays induce defect centres in glasses recognizable at the brownish colouring of the irradiated sites not shielded by the gold mask. In the UV/Vis absorption
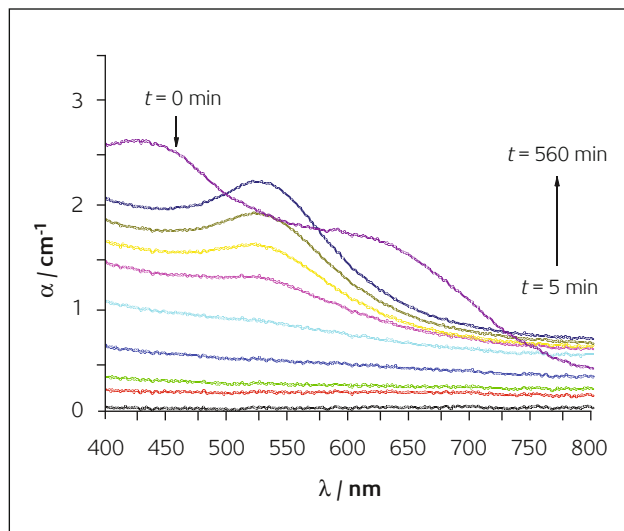

Figure 2
UV/Vis absorption spectra of a gold-ruby glass activated with synchrotron radiation and annealed at 500°C for 0, 5, 15, 45, 100, 160, 260, 360, 460, and 560 minutes
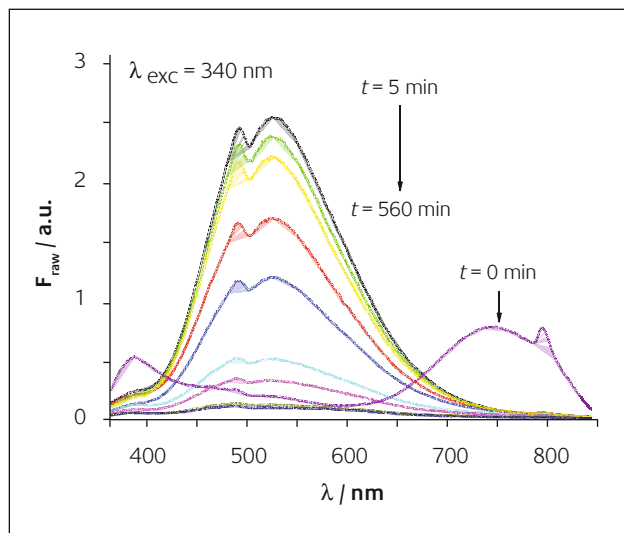

Figure 3
Uncorrected fluorescence spectra at room temperature of a gold-ruby glass activated with synchrotron radiation and annealed at 500°C for 0, 5, 15, 45, 100, 160, 260, 360, 460, and 560 minutes

spectrum peaks at 440 and 620 nm can be identified (figure 2). These bands can be assigned to the nonbridging oxygen (NBO) hole centres HC_1 and HC_2 (holes trapped in SiO_4 tetrahedrons with one and two nonbridging oxygen atoms, respectively) (9). Interestingly, a red luminescence of the irradiated pattern is observed under UV light excitation. In the fluorescence spectrum a peak at 745 nm can be recognized after excitation at 340 nm (figure 3).

After annealing for 30 minutes at 300°C the sample becomes transparent and the characteristic fluorescence cannot be detected any longer. In this way it should be possible to write (by activation), read (by UV excitation) and delete (by annealing) information in glasses. Thermal treatment leads to a recombination of electrons and holes and consequently the glass becomes colourless again. The coincidence of generation and deleting of both defect centre absorption and of luminescence suggests that the observed red fluorescence could be due to defect centres. Glinka et al. investigated the red photoluminescence of mesoporous silica by density functional calculations and attributed the emission between 1.0 and 2.1 eV to isolated bulk and surface nonbridging oxygen centres (10). But the nature of luminescence caused by defect centres in silicon dioxide and silicon is still a controversial field and an all-embracing discussion would go beyond the scope of this communication.

As reported recently thermal treatment of synchrotron activated gold containing glasses at 550°C for at least 30 minutes results in the growth of gold nanoparticles (6). These colloids have a characteristic size dependent surface plasmon resonance in the green part of the spectrum and hence structures appear ruby. For instance 45 minutes annealing at 550°C induces the growth of particles with an average radius of 3.2 nm, a standard deviation of 0.9 nm and a surface plasmon resonance wavelength at 549 nm. Whereas these glasses show no fluorescence, astonishingly a bright yellowish green luminescence is observed under UV excitation, when the samples are annealed for a shorter period of time, typically for 5-20 minutes at 550°C (figure 4). After this short annealing the glasses are still colourless and the "invisible" microstructures can only be seen by UV excitation. In the appropriate luminescence spectrum two overlapping peaks at 500 and 530 nm can be observed under excitation at 340 nm (figure 3).

To minimize the error of sample heating and cooling for quantitative luminescence and absorption measurements the annealing times were increased by choosing a lower temperature of 500°C. After 260 minutes of thermal treatment a slight peak in the UV/Vis absorption spectrum at 525 nm can be assigned to the gold surface plasmon resonance (figure 2). Further annealing is accompanied with an increase of this peak and can be interpreted in terms of the growth of gold nanoparticles.

Analysis of the appropriate luminescence spectra gives us the following results. The strongest emission peaking at 500 and 530 nm is observed after 5 minutes annealing at 500°C
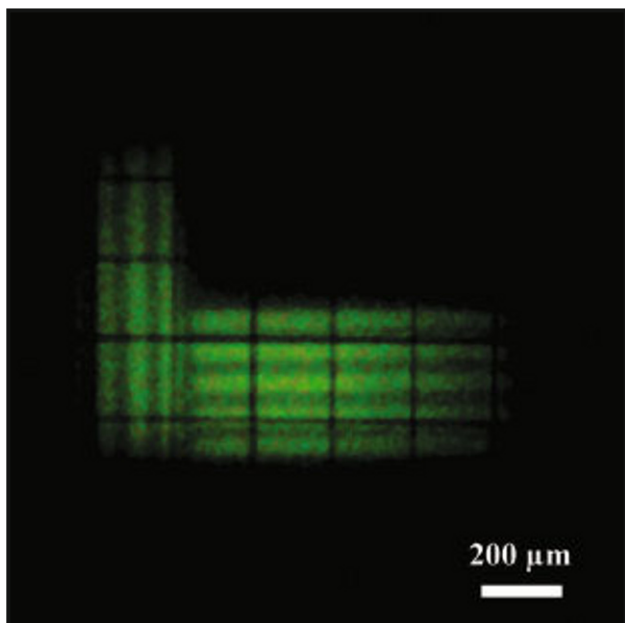
Figure 4

Confocal microscope fluorescence image at room temperature of an X-ray lithographically structured gold-ruby glass after annealing for 5 minutes at 550°C. The excitation wavelength is 366 nm. The width of lines and spaces is 40 µm
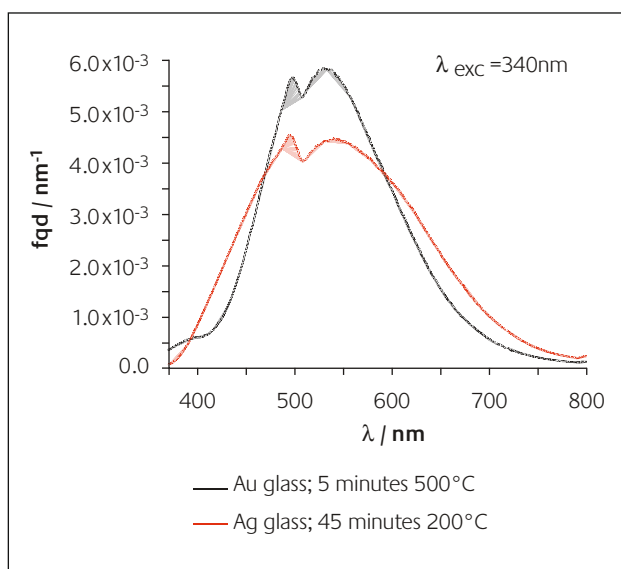

Figure 5

Fluorescence quantum distribution of gold and silver containing glasses activated with synchrotron radiation and subsequently annealed

(figure 3). Further thermal treatment results in a decreased luminescence and after 560 minutes only a very weak light emission can be determined (figure 3). These observations correlate very well with the increasing absorption. For the sake of interpretation it is helpful to compare the observed findings with experiments on silver doped glasses. The method of nucleation and growth of metal clusters in glasses with synchrotron radiation is applicable to samples containing silver, too. The only difference is the lower annealing temperature needed for particle growth due to the

higher diffusion constant of silver in glass. After activation of silver glasses with synchrotron light a weak yellowish white luminescence can be seen under UV excitation which is strongly enhanced after annealing for 45 minutes at 200°C. In the emission spectrum two peaks at 500 and 530 nm can be identified after excitation at 340 nm. Comparison of the fluorescence quantum distribution (calculated by dividing the fluorescence spectrum by the integral of the fluorescence spectrum) of both luminescent gold and silver containing glasses leads us to the conclusion that the observed luminescence mechanism is most probably the same (figure 5). Only a very weak photoluminescence is detected in just as treated reference glasses containing neither gold nor silver. Obviously we observe an intrinsic glass luminescence enhanced by gold and silver, respectively. This is in agreement with investigations of Krol et al., who reported on a fluorescence of femtosecond laser-modified glasses (11). Irradiation of fused silica with 130 fs laser pulses from an amplified Ti-sapphire laser operating at 800 nm results in a fluorescence of the laser written lines. They assign the observed emission peaking at 630 nm and excited at 488 nm to nonbridging oxygen hole centres. Furthermore this band is also detected when fused silica is irradiated with X-rays, neutrons or UV lasers (12). Hence we suppose that the photoluminescence of synchrotron activated soda-lime-silicate glasses can be attributed to silicate hole centres, too.

Conclusions

In our communication we describe the growth of gold clusters with tuneable radii by synchrotron X-ray activation of soda-lime-silicate glasses containing gold. For the first time we have shown that by implementing synchrotron X-ray lithography plasmonic or luminescent microstructures down to 5 micrometers can be written in glasses. Synchrotron activation induces a red photoluminescence of the irradiated structures, which vanishes after annealing the sample at 300°C. Thermal treatment for 5 minutes at 500°C causes a bright yellowish-green luminescence in the synchrotron irradiated, colourless, gold containing glasses. This way "invisible" information is stored into the samples, which can be read out easily by UV excitation and fluorescence detection. The observed photoluminescence, possibly enhanced by very small gold clusters or atoms, is assigned to silicate hole centres. Colourless microstructures turn ruby after further annealing at 500°C due to the surface plasmon resonance of gold nanoparticles. It is very well conceivable that writing, reading and deleting emissive and absorptive structures in gold-ruby glasses with the described technique could be applied in remarkably stable optical storage media. In the future it should also be possible to implement the process in the production of micro-optical devices like photonic crystals for telecommunication

wavelengths or Bragg gratings. ther applications like as sensor materials could base on surface plasmon resonance (SPR) spectroscopy, the surface enhanced Raman scattering (SERS) or the metal enhanced fluorescence (MEF) effect.

About the authors

Maik Eichelbaum is a PhD student in the group of K. Rademann, working on the generation and characterization of noble metal clusters in inorganic glasses.

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Acknowledgement

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