Chapter 3. Photomodification of single Ag nanoparticles embedded in soda-lime glass

In the last two decades growth of the interest to research on synthesis of composite materials containing metal nanoparticles is motivated by the rise of various potential applications in different fields of science and technology [3.1-3.3]. For instance, linear and nonlinear optical properties of such materials driven by surface plasma (SP) oscillations of the metal clusters offer the metalodielectric composites as promising media for development of novel nonlinear materials, nanodevices and optical elements. The SP resonance is very specific for different metals and strongly depends on size, shape, distribution and concentration of the nanoparticles as well as on the surrounding dielectric matrix. Thus, the laser-based techniques to modify shape and arrangement of the metal clusters [3.4-3.15] are of great interest since they provide a very powerful and flexible tool to control and optimize the linear and nonlinear optical properties of metalodielectric composites. Recently, it was discovered that a permanent transformation of initially spherical metal nanoparticles embedded in soda-lime glass into ellipsoidal (or more general, non-spherical) shapes can be made by irradiation with intense fs laser pulses near to the SP resonance [3.12-3.16]. Moreover, the dichroism in the spectra was strongly connected to the laser polarisation and inversely changed by irradiation in single-short and multi-short regimes [3.14]. However, the mechanism responsible for the anisotropic shape transformations of the spherical Ag nanoparticles seems to be very complicated and still needs detailed investigations.

In this chapter your attention will be focused on study of processes arising by interactions of intense fs laser pulses with single spherical Ag nanoparticles in soda-lime glass. Under “single nanoparticles” we consider a situation, when a volume concentration of silver inclusions is low enough and the collective interactions between nanoparticles can be neglected. The experimental results presented here include studies of intensity dependences of laser induced shape transformations of the silver nanoparticles, effect of the excitation wavelength, writing density and the temperature on the laser induced dichroism, dynamics of the laser induced modifications and luminescence study of modified composite glass. Interaction of intense fs laser pulses with host glass matrix resulting in ionization and colour center formation was also studied in this chapter.
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3.1 Transformation of the spherical shape of Ag nanoparticles: effect of the laser polarization, pulse intensity and wavelength.

As it was mentioned above, the recent investigations performed by M. Kaempfe et al. [3.12-3.16] demonstrate a dichroism in composite glass with initially spherical Ag nanoparticles induced by irradiation with intense fs laser pulses at wavelengths near to the SP resonance. Moreover, single-shot and multi-shot irradiation resulted in an inversion of the dichroism in extinction spectra. However, fs laser induced modifications of spherical Ag nanoparticles can be effected by various factors such as the laser pulse intensity, number of shots per spot, laser wavelength, temperature as well as size, distribution of silver clusters and glass matrix composition. In this part, we will consider effect of the laser pulse intensity, pulse writing density and excitation wavelength on the laser-induced dichroism in soda-lime glass containing spherical Ag nanoparticles.

For measurements of the intensity dependences we used a technique of space resolved transmission spectra described in details in the Chapter 2. In combination with laser beam profile measurements the space resolved spectra were correlated with local laser pulse intensities (see Chapter 2). Effect of the excitation wavelength on the induced modifications was studied using exposure of the broad fields on the samples described also in the Chapter 2. Irradiation was performed using Ti:sapphire mode-locking laser with regenerative amplification by 150 fs laser pulses in a spectral range of 267-800 nm. Furthermore, it has to be mentioned that the laser pulse intensity used in experiments was much below the damage threshold of soda-lime glass to be about of $1.5 \times 10^{14} \text{W/cm}^2$ [3.17-3.18].

3.1.1. The laser induced dichroism: effect of the laser pulse intensity and writing density on the anisotropic shape modifications.

In order to study the intensity dependences of the laser induced modifications in composite glass with spherical Ag nanoparticles the irradiation was carried out by

![Polarised extinction spectra of samples with Ag nanoparticles](image)

Fig.3.1. Polarised extinction spectra of samples with Ag nanoparticles: original sample and irradiated at 400 nm: a) in single shot regime, peak pulse intensity was 2.4TW/cm² (peak fluency 360 mJ/cm²); b) in multi-shot regime (100 pulses in single spot), peak pulse intensity was 0.42TW/cm² (peak fluency 63 mJ/cm²)
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150 fs laser pulses at 400 nm near to the SP resonance in single-shot as well as in the multi-shot mode. As it can be seen in Fig.3.1a, exposure in single-shot mode results in a splitting of the SP band of spherical Ag nanoparticles peaked at 418 nm in two polarization dependent bands slightly shifted toward long wavelengths: at 445 nm for p-polarisation (parallel to the laser polarisation); at 460 nm for s-polarisation (perpendicular to the laser polarisation). However, in order to induce visible dichroism we used the peak pulse intensity as high as 2.4 TW/cm² (spectra measured in the centre of a modified spot on the sample). For the sake of simplicity let us call such type of dichroism as “blue-side dichroism” (p-polarised SP band is shifted in blue side of the spectra relative to the s-polarised one).

At the same time, the multi-shot irradiation (a number of pulses usually >100 per spot) allows us significantly to reduce the laser pulse intensity to observe the anisotropy in the sample. Moreover, in multi-shot irradiation, as it’s shown in the Fig.3.1b, the SP band for p-polarisation is shifted towards long wavelengths up to 500 nm while s-polarised SP band is peaked at 400 nm, demonstrating inversion of the dichroism in comparison with the single-shot mode. Such type of dichroism we will call below as “red-side dichroism”.

Observed fs laser induced dichroism in nanocomposite glass with spherical Ag nanoparticles (red-side and blue-side as well) can be explained by anisotropic modifications of the shape of the silver clusters. Moreover, as it was shown in Chapter 1, the spectral gap between SB peaks in p- and s-polarizations is defined by the aspect ratio (length to width) of the pro-long metal clusters. In fact, the Transmission Electron Microscopy (TEM) (Fig.3.2) explicitly testifies formation of oblong uniformly oriented Ag nanoparticles in irradiated samples. Moreover, by single shot irradiation Ag nanoparticles have been aligned perpendicular to the laser polarisation (Fig.3.2B), while multi-shot mode resulted in elongation of silver clusters parallel to the electric field vector (Fig.3.2C). At the same time, in the single-shot as well as in the multi-shot irradiation a part of particles, as it can be seen in the fig.3.2D, did not change the form demonstrating only formation of aggregated small metal clusters in the surrounding and define the isotropic contribution in extinction spectra.

An interesting phenomenon of orientation rotation of the silver clusters by single-shot and multi-shot irradiation obviously represents the different polarisation dependent mechanisms resulting in anisotropic shape modifications of spherical Ag nanoparticles. Moreover, as it has already been mentioned, the pulse intensity in single-shot and multi-shot modes differs by factor of 6 and can apparently play a key role in generation of blue-side and red-side dichroism.
Indeed, a dependence of the SP maxima in polarised extinction spectra of modified samples on the laser pulse intensity presented in Fig.3.3 completely testifies our assumption. As it can be seen in the Fig.3.3A, the laser induced changes in the extinction spectra by single-shot irradiation were detected only by overshoot of the intensity threshold of approximately 0.2 TW/cm$^2$. Following increase of the pulse intensity leads to the shift of both p- and s-polarised bands towards long wavelength. Moreover, pulse intensities in the range of ~0.3-1.5 TW/cm$^2$ induce the weak red-side dichroism observed in multi-shot irradiation: p-polarised SP band is shifted a little bit farther towards long wavelengths relative to the SP peak for s-polarisation. Near to the 1.5 TW/cm$^2$ extinction spectra are isotropic and only higher intensities extinction spectra indicate the blue-side dichroism of the SP resonance. By intensity of about 2.4 TW/cm$^2$ we reach the maximal spectral gap between p- and s-polarised SP bands peaked at 445 nm and 460 nm, respectively (Fig.3.1a). Following rise of the pulse intensity led to the blue shift of both SP resonances with simultaneous bleaching and broadening of SP bands in the spectra indicating obviously destruction of the silver nanoparticles (Fig.3.4).

The multi-shot irradiation with writing density of 10 pulses per spot doesn’t change the intensity dependence of the induced dichroism (Fig.3.3B). As well as in the case of single-shot mode it can be characterised by two intensity ranges leading to the red-side (0.2-1.4 TW/cm$^2$) and blue-side (1.4-2.4 TW/cm$^2$) dichroism. However, in contrast to the single shot irradiation, increase of the number of laser pulses significantly improves the laser induced dichroism in glass with Ag
Irradiation of the samples with 100 pulses (Fig. 3.3C) doesn’t indicate any changes in extinction spectra for intensities below of 0.2 TW/cm², which is in the good agreement with single-shot and 10 shots irradiation. However, in contrast to the both previous cases, increase of the pulse intensity leads to a shift of s-polarised SP band in opposite directions relative to the original SP peak at 418 nm, while SP in p-polarisation moves towards long wavelengths. When the laser pulse intensity exceeds 0.6 TW/cm², the s-polarised SP band moves in the red spectral range leading to decrease in dichroic contrast (Fig. 3.4).

Furthermore, intensity dependence of the extinction spectra demonstrates destruction of the Ag nanoparticles upon exposure to intense fs laser pulses near to the SP resonance. As it can be seen from Fig. 3.4 laser induced dichroism in the composite glass is accompanied by broadening and bleaching of the SP bands in extinction spectra especially for high pulse intensities. The rise of the pulse number accelerates these processes. For instance, by irradiation with intensity of 2.4 TW/cm², increase in shot number (Fig. 3.4) results in the total disappearance of the SP peak in extinction spectra indicating destruction of the silver clusters. The broad residual absorption could be associated with the colour centre formation as well as by residual silver species and micro-defects induced in matrix.

Thus, the experimental data testify that the destructive processes are involved in the mechanism of the laser assisted deformation of the Ag nanoparticles. Moreover, the red-side and blue-side dichroism is defined rather by the laser pulse intensity indicating different intensity dependent mechanisms leading to the

Fig. 3.4 Extinction spectra of spherical Ag nanoparticles in soda-lime glass irradiated by 150 fs laser pulses at 400 nm with various peak pulse intensities.
formation of oblong Ag nanoparticles aligned parallel and perpendicular to the laser polarisation, respectively. The number of shots in such case enhances mostly effect of single shot modifications. It’s very important to notice that an intensity range between red-side and blue-side dichroisms results in isotropic changes of the extinction spectra, which could be related to modified nanoparticles with spherical shapes (Fig.3.2D). Thus, using the laser beams with Gaussian intensity distribution could lead to generation of nanoparticles with different types of modified shapes. However, even by top-hat intensity profiles enhancement and localisation of the light intensity in the glass sample could be additionally expected due to nonlinear interactions of laser pulses with intern microdefects and inclusions in the glass resulting in inhomogeneous intensity distribution in excited volume.

The formation of the small silver clusters in the surrounding of the distorted nanoparticle, which can be seen in TEM pictures (Fig.3.2), also testifies the destruction of the silver clusters. Moreover, the red shift of the SP peaks in extinction spectra for the pulse intensities higher as 0.5-0.6 TW/cm$^2$ could be caused by the dipole-dipole interactions between distorted silver nanoparticle and surrounding metal clusters. In the range of 0.2-0.6TW/cm$^2$ SP bands of modified samples represent shift in opposite directions relative to the original SP band of spherical nanoparticles peaked at 418 nm. The rise of the pulse number in this case increases first the spectral gap between s- and p-polarised SP bands and then the system reach a steady state without any following spectral alterations. Obviously, under these circumstances induced red shift of the SP resonance for p-polarization far away from the excitation wavelength restricts the excitation of SP and following elongation of the silver clusters.

3.1.2 Angular dependences of the laser induced dichroism.

As it has been shown above, the fs laser irradiation of Ag nano-spheres near to the SP resonance induces the elongation of the cluster shape. However, presented transmission electron microscopy does not answer a question, whether fs laser pulses result only in plain shape transformations (elongated disks) or silver nanoparticles have a form of spheroids (ellipsoids). In order to clarify this point, we performed a series of irradiations with incident angle about of 60 deg. Irradiation was carried out

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Fig.3.5. Extinction spectra of the glass samples with Ag nanoparticles: black solid line – original sample with spherical nanoparticles; dashed lines - irradiated at 400 nm with 150 fs laser pulses in multi-shot mode at normal incidence; solid lines - under incident angle of 60 deg. Laser polarization is parallel to the incidence plain. Scheme of the irradiation at an angle (top) and perpendicular (bottom) to the surface.
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at 400 nm in multi-shot mode, peak pulse intensity of ~ 0.5 TW/cm$^2$, and laser polarization parallel to the plane of incidence. As a result, irradiated samples demonstrated the laser induced dichroism, which was strongly dependent on the angle of observation. For instance, extinction spectra measured in direction perpendicular to the surface of the sample (solid line spectra in Fig.3.5) indicate in s-polarisation a SP band peaked at 380 nm, while two resonances can be seen in the p-polarisation centred at 380 nm and 510 nm. Change of the observation angle leads to the alteration of the extinction spectra. At angle near to the 60 deg (incident angle by irradiation) the extinction spectra are analogous to the case of the irradiation at normal to the surface: p-polarisation demonstrates single SP band at 510 nm (dashed spectra) and SP band in s-polarisation is centred at 380 nm. At the same time, the irradiated sample looks to be isotropic by observation at approximately -30 deg (approximately perpendicular to the direction of the irradiation). Such angular behaviour of the extinction spectra could be explained by formation of elongated silver nanoparticles uniformly oriented at an angle to the surface but parallel to the laser polarisation (Fig.3.5). In this case, the short wavelength maximum in the spectra for p-polarisation can be associated with the third axis of the cluster in direction of the laser beam propagation. Moreover, from the spectral positions of the short wavelength SP bands in s- and p-polarisations (peak at ~ 380 nm) we can conclude that two small axis are almost equal. In other words, the fs laser pulses cause transformation of the metallic nanospheres in spheroids.

On the other hand, if the laser polarization is perpendicular to the plain of incidence (actually parallel to the surface), extinction spectra don’t demonstrate the short wavelength peak in p-polarisation and are similar to the spectra at normal angle irradiation indicating elongation of the nanoparticles along to the surface.

Therefore, we can conclude here that elongation of the Ag nanoparticles is strongly defined by the laser polarization and variation of the laser incident angle allows to produce spheroids with any given orientation in the glass.

3.1.3 Subsequent modifications by multicolour irradiation.

In this paragraph, we continue the study of the fs laser assisted modifications of Ag nanoparticles in soda lime glass. In particular, we will consider the excitation of silver clusters at different wavelengths affected on the induced dichroism. Foremost, we have to notice that all observed induced anisotropic modifications of Ag nano-spheres described above occurs by excitation of Ag nanoparticles at wavelengths near to the SP resonance. The spectral gap between the SP bands in polarized spectra, which is defined by the aspect ratio of the elongated clusters, can be tuned by variation of the peak pulse intensity and/or by the writing density (number pulses per spot). However, increased pulse intensity besides with the spectral shift leads to the destruction of the silver nanoparticles and bleaching of the SP bands, what actually undesirably decreases contrast of the induced dichroism. At the same time, shift of the SP band away of the laser wavelength upon multi-shot exposure to fs laser pulses with low peak intensity restricts the excitation of silver nanoparticles and the system comes to a steady state, where increasing number of pulses doesn’t evoke any alterations in the extinction spectra. The far range spectral shift of the SP band could be apparently achieved by tuning of the laser wavelength towards SP resonance resulting in subsequent modifications of Ag nanoparticles.
In order to testify our assumption a glass sample with spherical Ag nanoparticles was irradiated first at $\lambda = 400$ nm in multi-shot regime (peak pulse intensity about of 0.5 TW/cm$^2$, writing density about of 3600 pulses per spot). As can be seen from Fig. 3.6 the original plasmon band peaked at 413 nm (solid line) is split into two polarization dependent bands (dashed curves) at 390 nm and 480 nm for s- (perpendicular to the laser polarization) and p - polarization (parallel to laser), respectively. These two bands are attributed to SP resonances along short and long axis of the modified (oblong) silver clusters, which have a preferential orientation parallel to the laser polarization. The same area of the sample was then irradiated at 550 nm with appropriate laser polarization for excitation of SP in the absorption band centered at 480 nm (laser polarization parallel to the long axis of the oblong silver cluster). This leads to a further modification (Fig. 3.6) and additional red-shift of the SP band corresponding to the long axis of the modified nanoparticles (p-polarization) to 630 nm. At the same time, a blue-shift of the absorption peak in s-polarization to 360 nm indicates an increase of the aspect ratio of the ellipsoids. On the other hand, appearance of the second peak at about of 412 nm in p-polarization can be attributed to a quadrupole contribution in the SP resonance. It should be noticed here that irradiation of the modified (ellipsoidal) as well as of the original (spherical) Ag nanoparticles under the same circumstances (peak pulse intensity, writing density) but at wavelengths sufficiently far away from the SP resonance (transparent spectral range) did not evoke any measurable extinction changes.

3.1.4 Modifications induced by fs laser pulses at 267 nm (interband effect).

Silver nanoparticles demonstrate an additional absorption band in the UV spectral range with maximum of ~ 310 nm corresponding to the interband transitions of the electrons.
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(see Chapter 1). Thus, irradiation of composite glass with embedded Ag nanoparticles at 267 nm (the sum frequency of SH (400 nm) and fundamental radiation (800 nm)) with peak pulse intensity of \( \sim 0.33 \) TW/cm\(^2\) (energy fluency of 49 mJ/cm\(^2\)) and writing density of \( \sim 10^4 \) shots/spot leads to transformation of the extinction spectra. In turn, as it can be seen in Fig.3.7, the intensity of the SP band decreases by the factor 3 and at the same time demonstrates induced dichroism: p-polarised absorption band shifts towards long wavelengths up to 421 nm, while absorption maximum for s-polarisation moves to 407 nm. Like in the case of excitation near to the SP resonance, such weak dichroism could be associated with Ag nanoparticles elongated in direction parallel to the laser polarisation. On the other hand, bleaching of the SP band in the spectra indicates destruction of the silver clusters upon exposure to UV laser pulses. However, it’s still a question, if the observed modifications are caused by excitation of the Ag nanoparticles in interband or fundamental absorption in the soda-lime glass plays here a role.

3.1.5 Femtosecond laser induced dichroism in composite glass with spherical Ag nanoparticles: first summary of the experimental data.

As it was discussed already in Chapter 1, fs laser pulse with moderate pulse energy can have extremely high peak intensity. In other words, electric field amplitude of the electromagnetic wave becomes very high in magnitude. Under these circumstances, exposure of a medium to the laser pulses could result in various nonlinear phenomena and even evoke structural modifications caused by multiphoton and tunnel ionisation. In Chapter 1 it was mentioned that the SP resonance of the metal nanoparticle is responsible for the local field enhancement in vicinity of the cluster, what in turn enhances the nonlinearity of the composite medium.

The experimental data presented above consider shape transformations of the spherical Ag nanoparticles in soda-lime glass upon exposure to fs laser pulses at wavelengths close to the SP resonance. As it was demonstrated, all observed laser induced modifications occur only in the given laser pulse intensity range (>0.2 TW/cm\(^2\)). Moreover, so called “red-side” and “blue-side” dichroism or in other words orientation of the modified silver clusters parallel or perpendicular to the laser polarisation is defined by the laser pulse intensity used for irradiation of the sample. The writing density (number pulses per spot) results in the accumulation of the induced modifications. However, it’s quite obvious that by the multi-shot irradiation the laser induced spectral changes are playing a feedback role and restrict modification of the cluster shape. For instance, shift of the SP band towards long wavelengths for p-polarisation (red-side dichroism) is obviously limited by decreasing absorption from pulse to pulse at the excitation wavelength. Thus, for the laser pulse intensities less as 0.6 TW/cm\(^2\) modifications reach a steady state when following rise of the pulse number doesn’t indicate some spectral alterations. However, tuning of the laser again towards the SP resonance stimulates subsequent modifications.

Observed anisotropic shape modifications are strongly combined, as it was demonstrated, with the laser polarisation indicating obviously nonlinear interaction of the SP with intense laser electromagnetic fields. In other words, the processes, which define a preferable orientation of the nanoparticles, should occur at time scales about of the laser pulse duration. At the same time, the thermal effects induced by the laser excitation of spherical Ag nanoparticles can only result in isotropic changes. Moreover, the experimentally observed fading of the SP band in extinction spectra...
with increase in peak pulse intensity allows us to suppose that partial destruction or dissolution of Ag nanospheres is involved in the shape modification mechanism.

It’s well known, that interaction of metal nanoparticles with intense laser pulses close to the SP resonance leads to the enhancement of the photoelectron emission from the cluster surface [3.19-3.29]. Even excitation of composite glass with Ag nanoparticles by ns laser pulses near to the SP causes a destruction of metal clusters accompanied by enhanced photocurrent [3.19] indicating a photovoltaic effect. Thus, it rather plausible to assume that interaction of intense fs laser pulses with silver inclusions in soda-lime glass results in SP assisted ionisation of metal clusters leading to the shape deformation and dissolution of the Ag nanoparticles. Moreover, by excitation of the SP with intense fs laser pulses the photoelectrons driven by the field on the surface of the metal nanoparticle, i.e. the superposition of the external field and induced polarisation, could assign the preferential direction for the modifications.

The laser pulse intensity of about 0.2 TW/cm\(^2\) (the threshold of the laser assisted modifications in the composite glass with Ag nanoparticles) could result in the photoionization of the silver clusters as well as glass matrix caused by multiphoton absorption. Moreover, such intensity corresponds to the electric field amplitude of electromagnetic wave to be in order of 6.1x10\(^6\) V/cm. Taking in to account the fact that excitation of Ag nanoparticles was performed near to the SP resonance, the enhancement of the local field in several orders of magnitude in comparison with incident wave makes the tunnel ionization probable.

On the other hand, it’s quite obvious that the oblong shape of the Ag nanoparticle is fixed by surrounding solid matrix. Heating of the sample exposed by fs laser up to 600 °C corresponding to the transition temperature in soda-lime glass causes a restoration of spherical shape of the modified Ag nanoparticles [3.14]. This allows us to assume that the fs laser assisted modification occurs under temperatures below of transition point. Otherwise, if the laser pulses result in the melting of the surrounding glass, keeping of the anisotropic shape by Ag nanoparticle is improbable.

Furthermore, the intense laser radiation can cause also the ionization of the glass matrix leading to structural transformations in it. Moreover, as it will be shown after, the soda-lime glass exposed to the fs laser pulses reveals an induced dichroism in visible spectral range caused by colour center formation. This can affect the electric permittivity of the glass and influence on the SP resonance of the incorporated metal clusters.
3.2 Modification of soda-lime glass by 150 fs laser pulses at 400 nm. Colour centres in the glass.

It is known that the laser intensities of about $10^{12}$ W/cm$^2$ lead to spectral changes in the transparent soda-lime glass caused by formation of color centers [3.30-3.32]. Moreover, generation of the color centers is characterised by the dielectric constant changes and can affect the position of the SP resonance in the extinction spectra of the composite glass. At the same time, ionization of the glass matrix and color centers formation can be involved in the processes of the shape modification of Ag nanoparticles.

Color center formation has been known since the XIX century and was extensively studied by exposure to $\gamma$-rays, UV radiation [3.33] as well as to intense laser pulses [3.30-3.32]. Whereas optical damage in glass is characterised by the formation of plasma and irreversible structural dislocations, the color centers formation takes a form of uniform slight discoloration of the medium through which the beam has been passed. The intern defects in the glass matrix or crystal (vacancies, interstitial ions and impurity ions of wrong valence) are characterised by an effective charge, which is able to attract and bind electrons and positive holes, which have been released in the matrix by exposure. Most of the electrons quickly recombine with the holes, that is, the electrons fall back into the stripped ions and reconstitute the normal ions. If before the recombination a free electron wanders near an interstitial cation or an anion vacancy, this positively charged defect can trap the electron in its Coulomb field. The positive holes that escape early annihilation also wander through the glass and are trapped at negatively charged defects, such as cation vacancies or interstitial anions. Moreover, trapped electrons or holes do not annihilate the charge of the defect but are only overlapping the surrounding of the vacancies or ions to an appreciable extent. Such trapped-electron or trapped-hole centers can be destroyed by warming the sample or by illuminating it with light of the appropriate wavelength. However, trapping of electrons by metal cations in the matrix leads to the reduction processes [3.35] and can bring even to a precipitation of metal colloids [3.32-3.34]. In such case, coloration in visible spectral range is determined by the SP band of metal clusters. In contrast with trapped electron and hole centers, which were discuss above, colloids mostly don’t demonstrate a thermoinduced bleaching in extinction spectra.

It should be mentioned that the concentration of the defects playing the role of trapping centers, strongly depends on composition of the glass. Thus, in the single component glass such as SiO$_2$ the substitution in the glass “random network” of Al$^{3+}$ for Si$^{4+}$ results in the creation of O$^{2-}$ vacancies or the simultaneous incorporation of aluminium cation interstitially playing a role of electron trapping centers. Formed charge imbalance in the matrix can be partially compensated by non-bridging oxygen contained in alkali silicate glasses in sufficient amounts. The non-bridging oxygen atoms together with cation vacancies are responsible for formation of hole-trapping centers in soda-lime glass [3.36].
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Thus, formation of color centers requires a generation of mobile charge carriers in the glass via the photoinduced excitation of electrons from the valence band of silicate glass to the levels situated above the electron mobility threshold (Fig. 3.8). For alkali-silicate glasses this threshold is placed in the region of the fundamental absorption age ($E_i \sim 5.4\text{eV}$) formed by transitions between levels in quasimolecular complexes $\text{Si-O}^\cdots\text{Na}^+$ (L-centers). Nonbridging oxygen defects $\equiv\text{Si-O}^-$ in silica are responsible for $4.8\text{eV}$ absorption [3.36]. Hence, exposure of glasses to radiation with photon energy less than intrinsic absorption age cannot cause photoionization of glass matrix. However, irradiation with high power laser pulses with $h\nu < E_i$ causes the multiphoton ionization of the glass matrix and formation of color centers [3.30-3.32]. On the other hand, sensitivity of the glasses can be significantly enhanced by impurities incorporated in the glass (like $\text{Ce}^{3+}$, $\text{Fe}^{2+}$, $\text{Tb}^{3+}$, $\text{Eu}^{3+}$ and so on), which form intermediate electron energy levels in the band gap of the glass matrix. Hence, ionization of impurities in the photosensitive glasses requires lower photon energies to induce electron transitions from intermediate energy levels in conduction band. In turn, the metal inclusions with Fermi energy level placed between valence and conduction bands can play a role of donor of electrons.

In our experiments, the original glass substrate (72.47 SiO$_2$, 14.36 Na$_2$O, 0.7 K$_2$O, 6.1 CaO, 4.05 MgO, 1.49 Al$_2$O$_3$, 0.133 Fe$_2$O$_3$, 0.131 MnO, 0.37 SO$_3$, weight %) used for Na-Ag ion-exchange and Ag nanoparticles preparation was irradiated by 150 fs laser pulses at 400 nm with peak pulse intensity about of $2.4\text{TW/cm}^2$. Irradiation was performed in multi-shot mode with writing pulse density of approximately $4\times10^3$ pulses per spot. As it can be seen in the Fig 3.9, the original glass sample is absolutely transparent in visible spectral range and demonstrates a wing of absorption band centred in NIR about of 1100 nm and attributed to impurities of $\text{Fe}^{2+}$[3.34]. The irradiation with fs laser pulses leads to coloration of glass in whole exposed volume characterised by a strong rise of the absorption in UV and visible spectral range (Fig.3.9). The extinction spectra of exposed glass...
demonstrate two broad absorption bands centred at 430 nm and 640 nm corresponding to the trapped hole color centers \( (\text{H}_2 \text{ and } \text{H}_4) \) \([3.31-3.35]\). The broad spectra in visible region as well as the absorption in UV can be associated with contribution of other types of trapped electron and hole centers presented in the Table 3.1.

Table 3.1 Spectroscopic parameters of the absorption bands of intrinsic Color Centers in Soda Lime Glass (according to Ref. 3.34)

<table>
<thead>
<tr>
<th>Peak Position, eV</th>
<th>Peak Position, nm</th>
<th>Halfwidth, eV</th>
<th>Charge State</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>1380</td>
<td>0.4</td>
<td>+</td>
<td>( \text{H}_1 )</td>
</tr>
<tr>
<td>1.6</td>
<td>770</td>
<td>0.7</td>
<td>-</td>
<td>( \text{E}_1 )</td>
</tr>
<tr>
<td>2.0</td>
<td>620</td>
<td>0.5</td>
<td>+</td>
<td>( \text{H}_2 )</td>
</tr>
<tr>
<td>2.1</td>
<td>580</td>
<td>0.8</td>
<td>-</td>
<td>( \text{E}_2 )</td>
</tr>
<tr>
<td>2.4</td>
<td>517</td>
<td>0.45</td>
<td>+</td>
<td>( \text{H}_3 )</td>
</tr>
<tr>
<td>2.85</td>
<td>435</td>
<td>1.1</td>
<td>+</td>
<td>( \text{H}_4 )</td>
</tr>
<tr>
<td>3.2</td>
<td>388</td>
<td>0.45</td>
<td>-</td>
<td>( \text{E}_3 )</td>
</tr>
<tr>
<td>3.7</td>
<td>335</td>
<td>0.8</td>
<td>-</td>
<td>( \text{E}_4 )</td>
</tr>
<tr>
<td>4.1</td>
<td>302</td>
<td>0.9</td>
<td>+</td>
<td>( \text{H}_5 )</td>
</tr>
<tr>
<td>4.75</td>
<td>261</td>
<td>0.9</td>
<td>+</td>
<td>( \text{E}_6 )</td>
</tr>
<tr>
<td>5.2</td>
<td>238</td>
<td>1.05</td>
<td>-</td>
<td>( \text{E}_7 )</td>
</tr>
<tr>
<td>5.8</td>
<td>214</td>
<td>0.8</td>
<td>+</td>
<td>( \text{H}_8 )</td>
</tr>
</tbody>
</table>

Moreover, extinction spectra reveal an induced dichroism in the glass sample after irradiation by fs laser pulses indicating higher absorption in s-polarisation in contrast to the p-polarised spectra. This can be explained by anisotropic optical bleaching of \( \text{H}_4 \) centers associated with laser polarisation dependent reorientation of those centers demonstrated by Glebov et al. \([3.37]\). However, Glebov and co-workers demonstrated effect of polarised laser irradiation at 435 nm on color centers induced by UV light. In our case, irradiation of glass samples at 400 nm by 150 fs laser pulses results in formation of color centers via multiphoton absorption. The following interaction of the fs laser pulses with \( \text{H}_4 \) hole trapped centers owing to the absorption peak at \( \sim 420 \) nm causes the bleaching and reorientation of them.

The spectral modifications in the glass induced by exposure at 400 nm are stable at room temperature retaining coloration unchangeable up to several years. However, thermal development of the irradiated glass at 150°C for 3 hours leads to the fading of the induced absorption \((\text{Fig.3.9})\) indicating recombination of color centers.

Similar spectral modifications were observed by irradiation of glass at 267 nm \((\text{Fig.3.10})\). However, in comparison with excitation at 400 nm penetration depth of the laser at 267 nm is much lower due to strong absorption in glass and

![Fig.3.10 Extinction spectra of soda-lime glass before and after irradiation by 150 fs laser pulses at 267 nm](image)
formation of color centers, which occurs only in the thin surface region. In the spectra two absorption peaks at 420 nm and 620 nm attributed to the hole trapped centers can be still resolved but their contribution in the spectra is much lower in comparison with the 400 nm excitation. This indicates apparently decrease of the proportion of the hole and electron trapped centers, which for example could be explained by contribution of Fe$^{2+}$ (absorption peaks at 4.4eV and 5.1eV) to generation of free electrons by excitation at 267 nm (4.7eV) [3.32, 3.35, 3.38, 3.39]. It’s well known that electron trapped centers are not stable at room temperature and the coloration in the glass induced at 267 nm disappeared in couple of days, while absorption bands formed by exposure to 400 nm were relative stable at 20 °C and bleaching was activated at 150 °C. Moreover, irradiation at 267 nm doesn’t demonstrate the anisotropic modifications of the soda-lime glass, which support the assumption of the polarisation dependent bleaching of the hole trapped centers by exposure to 400 nm.

In summary, the irradiation of the soda-lime glass with 150 fs laser pulses at 400 nm, below the fundamental absorption edge, results in multiphoton ionization of glass matrix and in the formation of trapped electron and hole color centers indicating induced absorption in UV and visible spectral range. Moreover, observed laser polarisation dependent dichroism in modified glass was associated with anisotropic bleaching and reorientation of the hole trapped centers H4. Trapped color centers are not stable to the heating and temperature treatment at 150 °C for 3h results in discoloration of the exposed region. Thus, obtained data indicate that the laser pulse intensities typical for Ag nanoparticle modifications at 400 nm also leads to the structural anisotropic transformations in the host matrix. In turn, effect of color centers formation on the extinction spectra of modified samples containing Ag nanoparticle can appear in two ways. First, induced absorption spectra of color centers in composite glass add to the absorption of silver clusters. Second, the color centers situated near to the surface of Ag nanoparticle increases the polarizability of the surrounding and will affect the surface plasma oscillations via dipole-dipole interactions as well as via influence of static effective charge redistribution shifting the SP peaks toward long wavelengths. Moreover, taking into account that the irradiation of Ag nanoparticles embedded in the glass was carried out near to the SP resonance, the enhancement of the local electromagnetic field can result in acceleration of the ionisation of the matrix near to the surface of metal cluster leading to formation of color centers, defects and even high ionised plasma (if the magnitude of the field is high enough) in the surrounding.
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3.3 Effect of the temperature on the laser induced modifications of Ag nanoparticles.

As it was shown in section 3.1, excitation of spherical Ag nanoparticles in soda-lime glass at SP resonance by intense fs laser pulses results in polarization dependent shape elongations. However, the mechanism of this laser induced deformation has not yet been elucidated in detail. A crucial question in this context is the possible ionization of the nanoparticles by intense femtosecond laser pulses. Moreover, as it was demonstrated in the Section 3.2, fs laser pulses at 400 nm with intensities exceeding the threshold of the laser induced modifications of the composite glass can stimulate the multiphoton ionization in the host glass matrix. This results in generation of trapped electron and hole color centers responsible for the induced absorption and dichroism in visible spectral range. Thus, the processes of color center formation could also be involved in the mechanisms of shape transformation of Ag nanoparticles. In turn, the color centers evoke modification of dielectric properties of the surrounding of the silver clusters and could affect on the surface plasma oscillations. Moreover, since the color centers are not stable by increase of the temperature, the temperature treatment of the exposed sample could reveal information according the laser assisted electron photoemission from Ag nanoparticles. On the other hand, the cluster ionization should lead to increase of silver ions content in the glass.

Since silver ions in glass as well as structural changes in the glass matrix can be identified by their characteristic photoluminescence, we have performed a series of luminescence measurements, combined with thermal treatment, of several samples: neat glass (i), ion-exchanged glass (ii), glass containing silver nanoparticles before (iii) and after (iv) laser induced deformation. The study is completed by extinction spectra demonstrating the effect of annealing on the latter type of samples. In the following it will be shown that the luminescence data provide interesting new information on the role of Ag nanoparticle ionization in the process of their laser induced shape modification.

3.3.1 SP bands modification by temperature treatment

The glass samples with spherical Ag nanoparticles used in the experiment were irradiated by 150 fs laser pulses at 400 nm in multi-shot mode. The peak pulse intensity was ~ 0.5TW/cm². Using X-Y translational stage a homogeneous field with size of 3x3 mm² was written with pulse density of ~ 4x10⁴ shots/mm².
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Under these conditions the effect of the laser irradiation on the extinction spectra, as shown in the Fig.3.11, is a splitting of the original plasmon band at 413 nm in two polarization dependent bands centered at 390 nm and 540 nm for s- (perpendicular to the laser polarization) and p-polarization (parallel to the laser polarization), respectively. As it was discussed in the Section 3.1, these two bands can be attributed to the SP resonances of the modified (oblong) silver clusters.

After irradiation, samples were heated in oven at 100°C, 200°C and 400°C and it was observed that the extinction bands due to the surface plasmon resonances of the elongated Ag nanoparticles are modified during temperature treatment (Fig.3.12). Upper, center and lower panel refer to 100°C, 200°C and 400°C, and the different curves (as specified in the legend of Fig. 3.12) represent the spectra measured before and after 5, 15, 45, 60, and 120 min of annealing. Common to all temperatures is a continuous reduction of the band width with simultaneous blue shift of both p- and s-polarization bands, accompanied by an increase of the maximum absorption strength. As it can be seen, the changes occur much faster at higher temperatures, so that, e.g., at 400°C no more modifications are observed after 45 min. In contrast to these findings, extinction spectra of non-irradiated samples with spherical Ag nanoparticles do not change at all during thermal handling.

Observed changes in the extinction spectra of the irradiated composite glass induced by temperatures much below the glass transition temperature to be about of 600 °C and silver melting point exclude the reshaping of the metal nanoparticles observed by M. Kaempfe [3.14] and can be interpreted in terms of modifications of the silver nanoparticle surrounding. Moreover, acceleration of the modification processes at temperature about of 100 °C allows us to assume a contribution of the trapped color centers, which are not resistant to the heating.

3.3.2. Luminescence study of the temperature induced modifications

The luminescence studies of the irradiated samples could help us in understanding of origins for the temperature induced modifications in the surrounding matrix and clarify the processes caused by interaction of Ag nanoparticles with ultrashort laser pulses.
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The first examples for luminescence spectra, as given in Fig.3.13, refer to the original glass (dash-dotted curve), ion-exchanged samples before annealing (dashed and solid curves), and an annealed, but not irradiated sample containing spherical silver nanoparticles (dotted curve); the excitation wavelength in all cases was 266 nm. Ag$^+$ ions in soda-lime glass are known to show upon UV-excitation a green-yellow luminescence due to the spin-forbidden electronic transition from the $^3$D manifold to the ground state $^1$S$_0$ [3.40,3.41]. Corresponding to this expectation the ion-exchanged sample 1 shows under excitation at 266 nm a luminescence band peaked at 540 nm (solid curve).

If this sample is being annealed in H$_2$ reduction atmosphere, the formation of Ag nanoparticles leads to a shift of the emission band to $\approx$ 520 nm (dotted curve), reflecting the decrease of the concentration of Ag$^+$ ions [3.41]. This interpretation is confirmed by the very good coincidence of this ('yellow') emission band with the spectrum of an ion-exchanged glass with Ag$^+$ ion concentration decreased by a factor of 10 (sample 2, dashed curve). At the same time, the Ag-Na ion exchange method leads to an inhomogeneous distribution of Ag$^+$ ions in the depth of the glass sample. Therefore, the shoulder observed near to 430 nm in the emission spectra can be explained by silver ions with lower concentration in the depth of the glass substrate [3.41].

The second, stronger emission band obtained from the sample containing spherical silver nanoparticles (peaked at 700 nm), was detected also from original clear glass (dash-dotted line). This band could be associated with nonbridging oxygen defects in the glass, which were studied in details in Ref. [3.42]. As it was mentioned in the Section 3.2, nonbridging oxygen anions =Si-O$^-$ are assigned as the cause of the 4.8 eV absorption and playing a key role in formation of hole trapped centers. Thus, illumination of soda-lime glass at 267 nm results in excitation of nonbridging oxygen anion and following electron transition from excited state on the energy levels of neighbouring electron trapping centers (Fig.3.14). Formed trapped
hole centers are in excited state and following transition in ground state energy level is accompanied by luminescence at 700 nm. However, electron and hole trapped centers are not stable and the system rapidly comes in the initial state. It is important to notice that the concentration of nonbridging oxygen centers is strongly dependent on impurities in the glass matrix [3,33]. It is rather plausible to assume that during the ion exchange process (which is connected with heating) most of these defects are ‘healed’, while reduction of the silver ions and aggregation to Ag nanoparticles may create new defects, in particular in the vicinity of nanoparticles. This scenario would explain the behaviour of the emission band at 700 nm.

When the sample containing silver particles is irradiated by intense 400 nm laser pulses in the above described way to modify the clusters, the luminescence observed upon excitation at 266 nm changes to the shape shown in Fig.3.15 as solid curve; compared to the emission spectrum before ‘destructive’ irradiation (dotted curve in Fig.3.13), mainly the intensity of the band around 700 nm is decreased. Thermal treatment of the sample (1 hour at 400°C) again increases the intensity of this luminescence band at 700 nm, which can be explained by modifications of the glass matrix. At the same time, the band attributed to the silver ions does not show significant spectral changes. So the experiments at 266 nm excitation wavelength alone can not prove the ionization of silver clusters during laser induced shape modifications.

We have performed additional luminescence experiments with an excitation wavelength of 400 nm, where the photon energy is too low to excite photoluminescence of Ag+ ions, but sufficient to observe luminescence around 600 nm due to very small charged clusters like Ag2+, Ag22+, Ag3+ and Ag32+ [3,40]. No noticeable luminescence intensity was observed from clear glass and samples containing silver nanoparticles, even if they have been irradiated by the intense pulses for deformation. Also heating of samples with spherical nanoparticles does not evoke the luminescence upon 400 nm excitation.

However, in case of previously irradiated samples the situation changes dramatically under thermal treatment: the Fig.3.16 shows the evolution of the luminescence spectra obtained from such a sample at 3 different temperatures (upper panel: 100°C; center panel: 200°C; lower panel: 400°C). The individual spectra are labeled with small letters (a) to (e) referring to 5, 15, 45, 60 and 120 minutes of annealing at the given temperature.
At all temperatures a broad emission band around 600 nm develops during heating, but on quite different time scales: at 100°C the intensity of luminescence rises for the first 15 min, then decreases again until it has vanished after 2 hours; with increasing time, the maximum of this luminescence band shifts from 540 nm to longer wavelengths. At 200°C the increase and following fading of the luminescence happens more rapidly and the equilibrium is achieved after 60 min; finally, at 400°C the emission reaches its maximum intensity within 5 min, and already after 15 min no measurable luminescence around 600 nm was detected any more. In addition, Fig.3.16 clearly shows that the maximum luminescence intensity is higher at higher temperatures. It is interesting to compare these spectra with one obtained from glass after Na-Ag ion exchange (sample 1), again with an excitation wavelength of 400 nm. As plotted in Fig.3.17, this sample with high Ag doping concentration yields a very similar strong luminescence band at 600 nm indicating the presence of the Ag$^{2+}$, Ag$^{2+}$, Ag$^{3+}$ and Ag$^{3+}$ species [3.40]. It is an obvious conclusion that the orange luminescence from irradiated samples containing deformed nanoparticles originates from those small silver ion complexes, which are being formed during heating of samples with high silver ions concentration. The position of the emission band of small silver clusters (Ag$\text{$_2$}$–Ag$\text{$_8$}$) depends strongly on their size and ionization state [3.43]. The emission band maximum is shifted to the red spectral range when the number of atoms in a cluster increases. Thus, the observed shape modifications of the emission band at 600 nm in the spectra of irradiated samples could be explained by inhomogeneous spectral broadening due to a wide distribution of silver species in size and charge (Ag$_n^{k+}$, n = 2, 3, ...; k = 1, 2, ...).
3.3.3. Effect of the temperature on the laser assisted modifications.

In the previous section, we demonstrated that the temperature treatment of the irradiated samples by fs laser pulses stimulates the spectral changes caused by structural modifications in the composite glass with silver nanoparticles. Obtained results raise a question how the temperature will effect on the irradiation procedure and laser induced modification of spherical Ag clusters. To answer this question the laser exposure of the glass samples with embedded Ag nanoparticles was performed at different temperatures. Irradiation by 150 fs laser pulses at 400 nm was carried out in multi-shot mode using the same technique and parameters as for the samples studied in the section 3.3.1. However, the peak pulse intensity here was about of 0.4 TW/cm².

As it can be seen in the fig.3.18, laser excitation at room temperature leads to the similar results reported above: SP band peaked at 413 nm splits in two polarisation dependent bands with maxima at 380 nm and at 510 nm for s- and p-polarisation, respectively. On the other hand, preheating of the sample up to 200 °C and following irradiation under the same circumstances did not demonstrate the induced dichroism in extinction spectra and led to an absolute bleaching of the original SP band, which in turn could be explained by total destruction of the silver clusters in the heated glass upon fs laser irradiation.

3.3.4. Interpretation and discussion of the temperature assisted effects.

The results presented above give evidence that Ag⁺ ions are produced in the glass matrix in the course of laser induced deformation of silver nanoparticles: the occurrence of a strong luminescence band around \( \lambda = 600 \text{ nm} \) under excitation at 400 nm, which was only observed for irradiated samples (containing oblong Ag nanoparticles), clearly indicates the formation of the mentioned small silver ion species \( \text{Ag}_2^+, \text{Ag}_3^+ \) etc.; as those can not be created from Ag clusters purely thermally, they are obviously due to clustering and partial reduction of previously produced Ag⁺ ions. It is quite reasonable that these ions are produced during the laser induced ‘destruction’ of nanoparticles, since enhanced photoelectron emission has been observed upon excitation of Ag nanoparticles by fs laser pulses near the SP resonance [3.19-3.29]. In the course of this ionization the positively charged core of ionized clusters will no longer be stable, and due to the Coulomb forces Ag ions will leave the clusters and form a local positive charge near to the surface of a particle. However, in our experiments using an excitation wavelength of 266 nm for
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Luminescence there was no unambiguous proof for an increase of concentration of free silver ions after high-intensity irradiation (compare Fig.3.14). The most plausible explanation for this problem is the fact that the emitted silver ions remain in the immediate vicinity of the silver clusters, producing a rather high local concentration of Ag\(^+\)-ions; for such a situation strong luminescence quenching was observed [3.41]. In addition, the non-irradiated samples containing Ag nanoparticles still show a relatively intense emission at 520 nm due to the residual free silver ions in the sample, which is present after annealing in reduction atmosphere (where the formation of silver species is limited and emission at 600 nm was not detected [3.44]) and formation of silver clusters, but also after laser irradiation and repeated annealing (Fig.3.14). So it is reasonable that silver ions produced during irradiation close to the silver particles do not cause remarkable changes of the Ag\(^+\)-ion luminescence band centered at 520 nm (under excitation at 266 nm).

Putting the above arguments together, it is obvious that the broadband luminescence observed after heat treatment around 600 nm (excitation at 400 nm) must be attributed to small silver ion species (like Ag\(_2^+\), Ag\(_3^+\), Ag\(_3^{2+}\)), which are produced from silver ions created near to the Ag nanoparticles during laser induced ionization and Coulomb explosion. This conclusion is supported by the fact that luminescence at 600 nm was not detected in original samples with spherical nanoparticles subjected to heating. At this point it should be mentioned that color centers, which appear in the original transparent soda-lime glass by intense laser irradiation at 400 nm, as it was discussed above, disappear completely after annealing at 150°C for 120 min. Apparently, heating initiates the dissociation of the electron trapping centers in glass and reduction of silver ions, and the consecutive formation of the small charged Ag clusters. This fact and the relatively low activation temperature of 100°C for modification processes allows us to suppose an influence of the trapped electron color centers on formation of silver ion species. When the annealing temperature is increased up to 200°C and 400°C, the dissociation of color centers is accelerated, and the evolution of the observed luminescence spectra reflects the formation and ripening of charged silver ion aggregates. Fading of luminescence with time is a result, apparently, of growth of the small ionized silver clusters playing the role of nucleation centers for silver colloids [3.40] and finally of their coalescence with the original silver particles (Ostwald ripening).

This interpretation is confirmed by the effects of the heating on the extinction spectra of irradiated samples with Ag nanoparticles, i.e., narrowing and blue-shift of the SP bands (Fig. 3.12), which are obviously caused by modifications in the surroundings of silver particles: after irradiation by intense laser pulses causing particle deformation, there will be silver ions near to the remaining particles, and photoelectrons caught by trapping centers in the glass matrix. While the silver ions in the vicinity of Ag particles may affect their plasma oscillation via a DC electric field, the photoelectrons caught in trapping centers in the glass could change the polarizability of the cluster surroundings and thus the effective dielectric constant of the matrix. Both effects will contribute to broadening and red-shift of the surface plasmon bands, where the broadening may also be due to the inhomogeneous distribution of local environments. Apparently, the effect of heating then is the dissociation of the electron trapping centers and reduction of silver ions, followed by aggregation of small ionic silver clusters. Finally, these silver ion species will diffuse back to the remainder of the original (disrupted) nanoparticle and reaggregate with it, probably forming larger species before their final coalescence. The latter can be concluded comparing the temporal evolution of both extinction spectra (Fig. 3.12)
and luminescence at 600 nm (Fig. 3.16) under temperature treatment: as long as the luminescence is rising, the extinction bands show only very weak changes; the more significant changes, in particular the increase of extinction strength, are observed when the luminescence is already decreasing or even practically vanished. This is most evident at the higher temperatures (200°C and 400°C); in the latter case no more spectral changes are observed after 45 minutes indicating that the surroundings of the Ag nanoparticles is in an equilibrated state already. For the lower temperatures the extinction spectra after 2 hours of heating differ from that one obtained at 400°C, and – in full agreement with the expectation for thermally activated processes – appear not to have reached their equilibrium situation yet.

Furthermore, fs laser induced ionization of the Ag nanoparticles is obviously responsible for the bleaching of the SP band observed by irradiation of the glass samples heated up to 200 °C. The fact is that an increase of the glass temperature stimulates high diffusion mobility of the silver cations. Thus, the silver cations ejected by the positive charged core are diffusing in the glass out from the Ag nanoparticle preventing the formation of the positive charged shall of the silver cations around the silver clusters and resulting in dissolution of them. This indicates that the local increase of the silver cation concentration in vicinity to the cluster surface are protecting the nanoparticles from total dissolution and are involved obviously in the processes of the shape modifications. Indeed, following reduction of the silver cations by emitted electrons in direction parallel to the laser polarisation and precipitation of the species in vicinity to the cluster core could result in the elongation of the Ag nanospheres.

As a prove of proposed mechanism of temperature induced alteration of extinction spectra a series of TEM images of irradiated samples before and after annealing at 300 °C for approximately 3 hours were recorded and presented in the Fig.3.19. As it was demonstrated above in the Section 3.1 and sown in the Fig.3.19A,D, irradiation of the samples by fs laser pulses near to the SP resonance leads to the formation of oblong as well as nearly spherical silver nanoparticles with surrounding small clusters. Here we have to point out that the aggregation of the small metal species could be caused by inescapable temperature increase due to
action of mechanical polishing and exposure to ion-beam during preparation of the samples over a long time for the TEM studies. As it was shown above, irradiated samples are very sensitive to the increase of the temperature and demonstrate changes in extinction spectra even at 100°C. Nevertheless, after temperature treatment irradiated samples are evidently (Fig.3.19 B,C,E,D) indicating modifications of the surrounding of distorted Ag nanoparticle: concentration of small silver clusters drastically decreases accompanied by their ripening; a little bit fare away from modified nanoparticle aggregation of small silver cluster were detected, which can form an anisotropic shape. The formation of the aggregates in the long ranges over the nanoparticle is indicating obviously generation and diffusion of silver cations during exposure to fs laser in glass matrix away from the hot metal cluster, which, in turn, reduced and agglomerated in silver species by following temperature treatment. According to the observed anisotropy of the species distribution around of modified elongated nanoparticle it’s rather plausible to assume that photoemission of electrons in the direction of laser polarization leads to a partial reduction of the silver cations and re-aggregation of silver atoms with disrupted silver cluster resulting in anisotropic distribution of the silver ions around of nanosphere. Thus, these high mobility active silver cations are diffusing without any obstacle in other direction. However, we have to notice, that the last assumption has to be proven carefully by the additional experiments. Nevertheless, these observations in general confirm the interpretation of spectral studies given above.

As a summery, by studying luminescence spectra, novel information has been obtained about the role of silver ions in the process of the fs laser pulse induced permanent deformation of spherical Ag nanoparticles in soda-lime glass to oblong ones. Samples with Ag nanoparticles show, after irradiation and only moderate temperature treatment at 100°C, a strong broad band luminescence (excitation wavelength 400 nm) centered at 600 nm, which can be attributed to small silver complexes Ag$_2^+$, Ag$_5^+$, Ag$_3^{2+}$. Additionally, temperature induced modifications of extinction spectra in the region of the SP bands indicate changes of the nanocluster environment by aggregation of the mentioned silver ion species. The fact that temperature treatment of original samples (containing spherical Ag nanoparticles, without irradiation) has no influence on the extinction spectra and also doesn’t evoke the luminescence upon 400 nm excitation, allows us to conclude that small silver ion complexes are formed from Ag$^+$ ions being created during fs laser irradiation by way of ionization and Coulomb explosion of silver nanoparticles. Actually, the increase of the local Ag$^+$ ion concentration near to the cluster, followed by reduction and cluster precipitation could play a key role in the processes of the fs laser induced modification of the shapes of Ag nanoparticles in soda-lime glass. Increase of the temperature of the sample during the laser irradiation leads to the total dissolution of the Ag nanoparticles in soda-lime glass, what in turn supports the proposed model.
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3.4 Dynamic of the laser induced modifications of Ag nanoparticles in soda-lime glass.

The ultrafast dynamics of SP resonance excitation by ultrashort laser pulses has been studied extensively in the last years, in particular in the low intensity regime, where any spectral changes are completely reversible [3.45-3.50]. On the other hand, as it was shown above, fs laser pulse with intensities higher as $10^{11}$ W/cm$^2$ reveal irreversible processes like cluster ionization and glass matrix structural modifications. Furthermore, these processes could play a significant role in transformations of the shape of silver nanospheres, which are responsible for induced dichroism of the SP bands in the extinction spectra. A first series of time-resolved single-color pump-probe experiments demonstrated a comparably slow relaxation process on a time scale of several 100 ps accompanying the deformation of Ag nanoparticle embedded in soda-lime glass by laser intensities about of 16.7 TW/cm$^2$ (energy fluency of 2.5 J/cm$^2$) in single shot mode [3.51]. However, laser pulses with peak intensity about of 2.4 TW/cm$^2$ reveal the ionization of the original soda lime glass and formation of the color centers resulting in darkening of the glass. It raises the question, whether ionization and formation of trapped centers can create a directional preference for material transport, which is necessary for the deformational process, but can only happen on clearly slower time scales.

Here we present results of time-resolved pump-probe experiment with 150 fs pump pulses at 400 nm and supercontinuum probe pulses giving important information about the possible source of the directional memory of the samples.

The first experiments were performed with low pulse intensities much below to the permanent modification threshold to be about of 0.2 TW/cm$^2$ (see Section 3.1). The fig. 3.20 shows some characteristic differential transient spectra measured on a sample with 50 μm thickness containing Ag nanoparticles, which indicate two regions of induced absorption (300-380 nm and 420-550 nm), and a region of bleaching between these two. In general, the three regions seem to evolve quite similarly as a function of time showing a fast rise and a slower decay on a time scale of several picoseconds.

For the detailed discussion of the time evolution it is more instructive to look at time-resolved data at some characteristic wavelengths.
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Fig. 3.21 Time dependence of the optical density changes in absorption spectra of glass containing Ag nanoparticles at different wavelengths. Excitation peak pulse intensity about of 2.6x10^9 W/cm^2 (energy fluence 0.4 mJ/cm^2).

As can be seen in the Fig. 3.20 and 3.21, at all wavelengths the signal rises for the first 0.3 ps. This is in general compatible with previous findings [3.52-3.54] in the weak perturbation regime, where the main changes around the SP resonance can be assigned to the non-instantaneous establishment of an electron temperature after excitation, i.e., the signal rise is determined by the thermalization time of the electron gas due to electron-electron, electron-surface and electron-phonon scattering. As the thermalization of this initially athermal electron distribution happens within a few hundreds femtoseconds for the amount of energy injected in our experiments, it’s easily understood that the signal rise more or less follows the integral over the pump-probe correlation. Following relaxation of the induced spectral changes with characteristic decay time about of 3.2 ps is associated obviously with transfer of electron energy to the lattice and later to the glass matrix. The transient spectra in the low perturbation regime can be described simply as a broadening and slight red-shift of the SP band caused by perturbation of metal complex dielectric constant. Our data are very similar to this behaviour at wavelength >380 nm, but exhibit an additional induced absorption at shorter wavelengths, which could be explained by an overall increase of the interband transitions due to the hot electron system, as has been observed previously [3.53].

Increase of the intensity of the pump pulse slightly modifies the differential absorption spectra (Fig. 3.22) indicating the rise of the optical density in the UV spectral region and simultaneous broadening and red shift of the growing absorption band in the other side of the SP resonance. At the first sight, such behaviour of the differential absorption spectra could be associated with strong heating of the electron.
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Fig. 3.23 Time dependence of the optical density changes in absorption spectra of glass containing Ag nanoparticles at 445 nm for different pump pulse intensities.

Fig. 3.24 Differentiation absorption spectra of the soda-lime glass for different time delays between pump and probe pulses.

gas induced by pulses with high energies. However, relaxation dynamic of the silver nanoparticles by excitation with the intense pump pulses (Fig. 3.23) reveals an appearance of the additional long time relaxation component with decay time up to ~1 µs. Moreover, increase of the pump pulse intensity up to 0.3 TW/cm² leads to the significant contribution of the long life absorption in the transient spectra. Here, we have to point out, that the modification threshold of the Ag nanoparticles in soda-lime glass was estimated in the Section 3.1 to be about of 0.2 TW/cm². So it may be concluded that observer long life absorption component at the intensities applied here are reflecting an additional physical process associated with the modification of Ag nanoparticles. An idea about the nature of this process can be acquired from a comparable experiment performed on the neat soda-lime glass substrate (Fig. 3.24), where the only difference is the significantly increased pump pulse intensity of approximately 1.2 TW/cm². Under such circumstances the initially transparent glass develops a weak, broad absorption with just the same time behaviour as extracted from the above data for the composite glass: at any position within that absorption band signal rises within 500 fs and then remains nearly constant or at latest decays only on a very slow time scale up to 1 µs (Fig. 3.25). The most obvious explanation for this transient spectra is the multiphoton ionization of soda-lime glass and
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the generation of trapped electron and hole color centers in the glass, which can produce, as it was shown in the Section 3.2, absorption bands in the visible spectral range, and are known to have rather long lifetimes up to being thermodynamically stable at room temperature. It’s plausible to assume that the long-lived absorption observed in the samples containing silver nanoparticles has the same origin (electron trapped in the glass matrix). The nanoparticles incorporated in the glass matrix can play in such case a role of short cuts for electron transitions in the composite glass reducing band gap between Fermi level of the free electrons in metal inclusion and conduction band of the glass matrix. Moreover, SP assisted local field enhancement in vicinity of the metal cluster can lead to the ionization of the surrounding matrix.

Obtained results find an excellent agreement with the experimental data presented in previous sections of this chapter. The measured dynamics of the SP excitations of Ag nanoparticles for different pump laser pulse intensities explicitly indicate appearance of the long time absorption component in transient spectra referred to the ejection of electrons and probably induced plasma in surrounding glass matrix leading to the following formation of the trapped color centers. It’s important to notice that this rise of absorption was observed at laser pulse intensities of about $10^{11}$ W/cm$^2$, what is in good agreement with the threshold of the laser induced permanent changes of extinction spectra of composite glass with spherical Ag nanoparticles determined in the Section 3.1. Furthermore, photoemission of electrons results obviously in positive charging of silver clusters and following Coulomb explosion with formation of free silver cations in surrounding, what, in turn, was manifested by the luminescence studies of irradiated glass samples with Ag nanoparticles presented in the Section 3.3.
3.5. Mechanism of the anisotropic shape modifications of spherical Ag nanoparticles in soda-lime glass upon fs laser irradiation.

The aim of this last section of the current chapter is to summarize experimental data and to propose mechanism of the SP assisted shape modifications of spherical Ag nanoparticles embedded in soda-lime glass by excitation with intense ultra-shot laser pulses. Performed investigations of the effects accompanying the anisotropic modifications in the composite glass allow us to manifest the following experimental facts:

1) the laser assisted modifications occur only by appropriate laser pulse intensity (higher than 0.2 TW/cm$^2$ by excitation at 400 nm) and exposure wavelength near to the SP resonance;

2) orientation of the modified silver clusters (parallel or perpendicular to the laser polarization) is defined by the laser pulse intensity used for irradiation; the number of laser pulses in this case plays mostly accumulative role;

3) fading and following total disappearance of the SP band in extinction spectra at higher peak pulse intensities indicate that the partial destruction or dissolution of silver cluster is involved in modification mechanism;

4) pump-probe experiments and luminescence studies testify the SP assisted electron photoemission and drastic increase of the content of silver cations in vicinity of disrupted nanoparticle; thus, the destruction of the silver nanoparticles occurs obviously due to Coulomb explosion during ionisation of the silver cluster;

5) resulting positive charged shell of the silver cation is playing apparently a key role in the shape modifications; thus, preheating of the sample up to 200°C increases the mobility of the silver cations and prevents formation of the cation shell in the vicinity of the cluster leading to total dissolution of the Ag nanoparticles upon laser irradiation.

Therefore, the experimental data testify rather complex mechanism of the fs laser assisted modifications of Ag nanoparticles incorporated in glass. Nevertheless, the whole process could in general be formulated as a consequence of the SP assisted electron photoemission (ionization), which leads to the following recharge in the matrix, Coulomb explosion of the metal nanoparticle and precipitation of Ag nanoparticle with asymmetric shape. Thus, the photoelectron emission from the metal cluster is the central point in the observed effects and deserves an attention of more detailed consideration.

3.5.1. Surface Plasmon assisted photoemission from metal nanoparticles.

Coming to the basics of the photoeffect, it’s well known that in order to induce a free electron carrier, the photon energy of the radiation have to overcome the electron work function, needed to exceed the binding energy of electrons with the surface (extrinsic photoeffect), or to excite transition of electrons from ground state into conduction band of dielectric (intrinsic photoeffect). However, as it has been already discussed in Chapter 1 and in Section 3.2, intense laser pulses even with hv less than the work function can evoke emission of electrons due to multiphoton, tunnel and even avalanche ionization.

In the last years the SP assisted photoelectron emission from supported Ag nanoparticles has been extensively studied upon excitation with intense ultrashort
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Therefore, the electron work function from the silver clusters defined as an energy gap between the Fermi level and the energy of the free electron in the vacuum is of about 4.3 eV [3.1,3.22,3.26]. Moreover, it was testified [3.29] that excitation near to the SP resonance extremely enhances the two-photon photoemission yield from the Ag nanoparticles.

In the composite glass, containing metal nanoparticles probability of the SP assisted photoemission can be strongly affected by a structure of electron energy manifold in the host matrix. In turn, an energy level scheme of the soda-lime glass with embedded Ag nanoparticles can be presented as a junction of the dielectric with a metal (Fig.3.26). The work function of the valence electrons in pure silica is about of 10.6 eV. Moreover, the edge of the fundamental absorption about of 9 eV in pure silica is caused by electron transitions from valence band in to conduction band. As it has already been mentioned in Section 3.2, impurities of the alkali cations in the soda-lime glass lead to shift of the fundamental absorption edge down to 4.8 eV. This is caused by transformations in the glass network and appearance of the nonbridging oxygen centers (Fig.3.26). Nevertheless, the lowest energy level of the conduction band in the glass is placed 1.6-1.7 eV below the energy of the free electron in vacuum. Thus, an energy gap between the Fermi level in the silver inclusion and conduction band in the glass is about 2.7 eV and consequently any radiation with photon energy >2.7 eV could evoke a tunnel transition of the electrons from the silver inclusion in to conduction band of the surrounding glass matrix, even by single photon absorption.

Excitation of the Ag nanoparticles near to the SP resonance (~3 eV) by the fs laser at 400 nm (3.1eV) leads to a non-thermal distribution of the electrons in the conduction band of the metal (the Fig.3.26, red dotted line). Since the maximal electron energy in these case exceeds the bottom of the conduction band of the matrix in 0.4 eV, the electron injection in the conduction zone of the glass could be possible. Here we have to point out that the photoemission opens up an additional channel for energy relaxation of the metal clusters. Following thermalization of the electrons with characteristic time of a few hundreds of femtoseconds (the Fig.3.26, green line) obviously restricts the photoemission processes. On the other hand, upon the two-photon plasma excitation the electrons overcome the ionization energy level and without any obstacles penetrate in the glass matrix. Even during thermalization the energy of the electrons could be high enough to jump in the conduction band of the glass. In turn, the injection of the electrons from metal inclusions in conduction band of the surrounding matrix is obviously the origin of a rise of conductivity in the
composite glass with Ag nanoparticles upon fs laser irradiation near to the SP resonance [3.19].

On the other hand, induced free carrier in the glass causes the broad absorption in the visible spectral range, which was observed in the composite glass as well as in the original soda-lime glass upon excitation with 150 fs laser pulses at 400 nm (see the Section 3.4). The fact that the threshold of the laser induced modifications is in quite good agreement with the laser pulse intensity indicating the free carrier absorption in the nanocomposite glass, allow us to associate the modification threshold with injection of photoelectrons in the glass matrix. During the plasma relaxation, the free electrons in the glass could be trapped by positive charged defects in the matrix leading to formation of color centers indicating long time relaxation component in the induced absorption spectra (see Section 3.4).

However, the proposed mechanism provides only isotropic photoemission of the electrons by the metal nanosphere. However, in the case of SP excitation we cannot exclude an effect of the local field enhancement in vicinity of the Ag nanoparticle. Moreover, by excitation with polarized light the E-field enhancement (Fig.3.27) occurs in special points on the surface [3.1, 3.2, 3.55]. The local field enhancement depends on the wavelength (on-resonance or off-resonance) and can reach several orders of magnitude higher than the incident field. In our experiment, the threshold of laser assisted modifications was determined to be about 0.2 TW/cm². This corresponds to the electric field amplitude of the electro-magnetic wave of about 6.1x10⁶ V/cm. The highest peak pulse intensity about of 2.4 TW/cm² gives the magnitude of the electric field amplitude of 9.45x10⁷ V/cm. Increase of the electric field in the vicinity of the silver cluster due to SP resonance could strongly suppress energy levels (see Chapter 1) on the metal-dielectric junction and induce effective electron carrier flow from the surface of nanoparticle parallel to the laser polarisation. The anisotropy in this case is determined by anomalous distribution of the local electric field over nanosphere (Fig.3.27). On the other hand, the electric field in the vicinity of the metal cluster could overcome a breakdown threshold of the glass resulting in the high density electron plasma formation and even ablation of the glass matrix on the poles of the nanosphere.

Therefore, the nonlinear photoionization of the silver nanoparticles are in good agreement with experimental data explaining the intensity threshold of the laser induced modifications and appearance of the broad band induced absorption with long relaxation time, which could be associated with the conduction electrons in the glass and following formation of the colour centers. In turn, as it was indicated by study of the temperature induced effects (the Section 3.3), the colour centers influence on the SP resonance of the Ag nanoparticle in extinction spectra apparently
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via dipole-dipole interactions. Moreover, the SP assisted local field enhancement can evoke an anisotropic photoemission of electrons from Ag nanoparticle resulting in anisotropic distribution of the induced defects (electron trapped colour centers) in surrounding glass matrix, which could play an important role in the anisotropic shape modifications.

3.5.2. Dipole-dipole interactions of the SP with induced free electron carrier in the surrounding glass matrix.

The laser induced ionization of the Ag nanoparticles results in generation of high density free electrons in the matrix, which in turn, after relaxation, lead to formation of the electron trapped colour centers in the vicinity of the Ag nanoparticle. The free electrons as well as the colour centers are indicating strong absorption at SP resonance and can result in resonant coupling of SP oscillations with matrix [3.56]. In this case, the dipole-dipole interactions between silver nanoparticle and surrounding media are responsible for an additional channel of SP damping and anisotropic energy transfer into matrix.

The dipole moment of the SP oscillation of metal nanoparticles with frequency of \( \omega_{SP} \) given as \( \mathbf{D}(t) = D_0 e^{i\omega_{SP}t} \) creates at distance \( r \) from the center of cluster an oscillating field \( \mathbf{E}(t, r) = E_0(r) e^{i\omega_{SP}(r-r/c)} \). The electric field amplitude \( E_0 \) could be expressed according to the Ref.[57] as:

\[
E_0(r) = \frac{3n(D_0 \cdot n) - D_n}{4\pi \varepsilon_0 \varepsilon' r^3},
\]

where \( \mathbf{n} \) is a unit vector in the direction of the radius vector, \( \varepsilon' \) is the real part of the complex relative permittivity of the surrounding medium \( \varepsilon = \varepsilon' + i\varepsilon'' = 1 + \chi' + i\chi'' \) (see Chapter 1, Eq.1.17). This electric field induces a polarization given as:

\[
\mathbf{P}(t, r) = \text{Re}(\varepsilon_0 \chi' \mathbf{E}(t, r)),
\]

where \( \chi' \) is the complex linear electric susceptibility of the medium. The average power absorbed per unit volume according to Ref.[58] can be expressed as:

\[
W = E(t, r) \dot{\mathbf{P}}(r, t) = -\frac{\omega_{SP} \varepsilon_0}{2} \chi'' \left| E_0(r) \right|^2.
\]

Substituting the Eq.3.1 in Eq.3.3 and after a couple elementary derivations we receive the angular dependent average power absorbed by the matrix:

\[
W(r, \Theta) = -\frac{\omega_{SP}}{32\pi^2 \varepsilon_0 \varepsilon'' r^6} \chi'' D_0^2 (1 + 3\cos^2(\Theta)),
\]

where \( \Theta \) is the angle between dipole of the SP oscillations and the radius vector. Thus, according to the Eq.3.4, if the absorption coefficient of the surrounding matrix
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is not equal to 0 at frequency of the SP resonance, the power flow is expected from the nanoparticle via dipole-dipole coupling of metal cluster and host matrix. Moreover, the energy absorption is more intense in direction of the laser polarisation (direction of the dipole orientation). Thus, strong interaction of the SP with the generated in the surrounding glass matrix free electrons and colour centers can result in highly anisotropic excitation of free electron carrier in the vicinity of the surface of nanosphere, which in turn could induce an anisotropic plasma formation, anisotropic temperature distribution and stress in the matrix.

3.5.3 Ionization assisted anisotropic shape transformation of spherical Ag nanoparticles in soda lime glass.

As it has been discussed above, excitation of the Ag nanoparticles with intense fs laser pulses near to the SP resonance induces the electron photoemission from the surface of the metal clusters. Moreover, electron flow in the direction of the laser polarisation (Fig.3.28A) and polarisation dependent resonant SP coupling with the glass matrix can result in formation of the high density electron plasma localised in glass near to the surface of the metal nanospheres in direction of the laser polarisation. Following relaxation of electrons leads to the formation of trapped electron centers concentrated mostly on the poles of the sphere. At the same time, resulting positively charged nanoparticles is not stable any more and eject silver cations driven by the Coulomb forces forming, as it was mentioned in section 3.3, a positively charged shell near to the disrupted cluster (Fig.3.28B). Moreover, the diffusion length of the silver cations in the glass matrix is restricted obviously by the mobility of Ag$^+$ and rapid thermal relaxation of the Ag nanoparticle. Here we have to point out that the energy transfer from the nanoparticle into the matrix results in considerable increase of the temperature in the cluster surrounding. However, the temperature should be below the transition temperature in the glass. Otherwise, the oblong shape of the cluster can not be fixed (it is proved by heating experiments at 600°C [3.14]). Nevertheless, under these circumstances the silver cations could be reduced by the electrons located in the matrix defects and evoke precipitation of silver aggregates in vicinity of the nanoparticle with following coalescence with the cluster. Moreover, the silver cations could play a role of electron trapping centers by the next laser pulse (Fig.3.28C) leading in intense precipitation and growing of the silver cluster in the direction of the laser polarisation. Apparently, this mechanism leads to the anisotropic distribution of the Ag$^+$ ions in direction

![Fig.3.28. Laser assisted shape modification of the metal nanosphere via ionization and precipitation.](image)


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perpendicular to the laser polarisation (Fig.3.28D), which was demonstrated by the experimental data (Fig.3.19B). Furthermore, the precipitation mechanism of the shape elongation is additionally approved by the laser assisted dissolution of the Ag nanoparticles in preheated sample up to 200°C. Increase of the temperature enhances the diffusion mobility of the silver cations in glass and apparently prevents formation of the cationic shell in vicinity of the metal cluster.

According to the proposed mechanism, formation of the high fraction of silver cations near to the cluster and photoemission of electrons in direction of the laser polarisation are responsible for precipitation of oblong silver nanoparticles embedded in soda-lime glass parallel to the laser polarisation.

On the other hand, this mechanism evidently works at laser pulse intensities slightly above the threshold of the laser induced modifications. Increase of the laser pulse intensity causes a rise of the temperature in the surrounding glass and diffusion mobility of the silver cations. This leads to expansion of the radius of the cationic shell and decrease of the concentration of Ag\(^+\)-ions near to the nanosphere. Thus, the precipitation and the anisotropic ripening of the Ag nanoparticles become less probable and extinction spectra as well as TEM demonstrate the isotropic changes (see Section 3.1). Moreover, if the laser pulse intensity is high enough, the plasma formation is probable on the interface of the glass and the silver inclusion in special points, where local electric field is maximal (on the poles of the sphere along to the laser polarisation). Moreover, the electron density of the electrons in the induced plasma is defined by the local electric field strength as well as by direct absorption of the laser radiation by free electrons and energy transfer from the nanoparticle to matrix via resonant SP coupling with the free electrons. The last two processes can induce very rapid increase of the electron density due to avalanche ionization of the glass. The following plasma relaxation leads to the transfer of the energy from electrons to the lattice (glass) on the time scale much faster than the thermal diffusion time. This can result in ablation of the material on the interface between glass and metal inclusion leading to partial destruction of the nanoparticle on the poles (Fig.3.29). Moreover, the shock due to expansion of the matrix evokes compression of the metal cluster in direction parallel to the laser polarisation.

In conclusion, in this section we discussed possible mechanism of the laser induced shape modifications of spherical Ag nanoparticles embedded in soda-lime glass. The main point of the proposed scenario is the SP assisted photoelectron emission of the electrons from the metal surface upon excitation with 150 fs laser pulses. The following development of the processes strongly depends on the applied laser pulse intensity: slightly above the modification threshold the Coulomb explosion and anisotropic ripening of the Ag nanoparticles results in elongation of the cluster parallel to the laser polarisation; intense laser pulses evoke the dense electron plasma on the glass-metal interface, which leads to ablation and compression of silver nanosphere resulting in orientation of the cluster perpendicular to the laser polarisation.