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ABSTRACT

An organic-inorganic synthesis route to Au-colloid containing, transparent SiO₂ coatings has been developed, using four different types of functionalized silanes as stabilizing ligands for the Au. By variation of the kind and the concentration of the stabilizing silane in the sol the onset temperature for the colloid formation varies between 100 and 300 °C and the final colloid radii can be controlled in a range between 3 and 30 nm after densification of the composite coatings on glass at 500 °C. The third order polarizability $\chi_m^{(3)}$ in the metal particles is one order of magnitude higher than in glass composites and exhibit a strong dependence on the ligand.

1. INTRODUCTION

Recently it was found that Au colloids can be generated in an organic-inorganic (Ormocer) matrix using functionalized silanes (amino- and thiosilanes) for the stabilization of Au³⁺-ions in the sol¹. Au colloids are formed by a combined UV and thermal treatment at about 200 °C that takes only a few minutes and leads to the densification of the Ormocer matrix simultaneously. Further investigations pointed out that the surface of the colloids is covered with the silanes that had been used for the ionic stabilization before, since the colloidal size decreases with increasing stabilizer concentration in the system². More recently³ it has been shown that this synthesis route leads to nonlinear optical ($\chi_m^{(3)}$) coefficients of $>10^{-6}$ esu that are about two orders of magnitude higher than those of Au colloids in glasses. The data may suggest that interface effects caused by the used ligand (aminosilane) are responsible for the increased nonlinear properties by an enhancement of the local field factor, as it is known for the resonant nonlinear optical (nlo) properties of CdS quantumdots⁴. On the other hand the high $\chi_m^{(3)}$ values were obtained from systems containing Au colloids with slightly distorted spherical shape which could be another reason for the increased $\chi_m^{(3)}$ values^{5, 6}. So it was very interesting to synthesize Au colloids in sol-gel coatings by routes leading to more spherical particles by thermally stimulated nucleation and growth, using surplus amounts of stabilizing ligands, as it has already been shown in the case of Pd⁷. This should allow to study the influence of more or less strong silane ligands on the Au colloid formation and their linear and nonlinear optical properties in a more systematic way.

2. EXPERIMENTAL

For the synthesis of gold-containing solutions 200 mg H[AuCl₄] \cdot 3H₂O was dissolved in 5 ml of ethanol and a functional silane of the group 3-amino propyl triethoxy silane (APTS), N-(2-amino ethyl)-3-amino propyl trimethoxy silane (DIAMO), trimethoxy silyl propyl diethylen triamin (TRIAMO) or 3-mercaptopropyl tri-

methoxy silane (THIO) was added in an equimolar ratio. The coating sols were synthesized from glycidoxy propyl triethoxy silane (GPTS) and tetra ethoxy orthosilicate (TEOS) in a molar ratio of 80 : 20 by refluxing a mixture of 160 g GPTS, 40 g TEOS and 27 g 0.1 M HCl in 240 ml of ethanol for 24 h at 80 °C. After that the gold-containing solution and surplus amounts of the appropriate functionalized silane were added and stirred for 30 min. at room temperature. Microscopy slides were dip coated with this sol using withdrawal speeds between 3 mm/s and 5 mm/s. After drying for 15 min. at 80 °C the coatings were densified at temperatures between 100 °C and 500 °C for 1 h using a heating rate of 1 K/min. The formation of gold colloids was monitored by UV-VIS spectroscopy (Bruins Omega 30) transmission electron microscopy (TEM, Jeol Jam 200) and WAXS (Siemens D 500). The coating thickness and the refractive index were determined by spectral ellipsometry (SOPRA ES 4G). The nonlinear optical experiments are performed by forward Degenerate Four Wave Mixing (transient laser induced grating⁸) with the copolarized beams of an excimer laser pumped dye-laser of 20 ns pulse duration (Lambda Physics) as described in [3].

3. RESULTS AND DISCUSSION

3.1. Preparation of the coatings

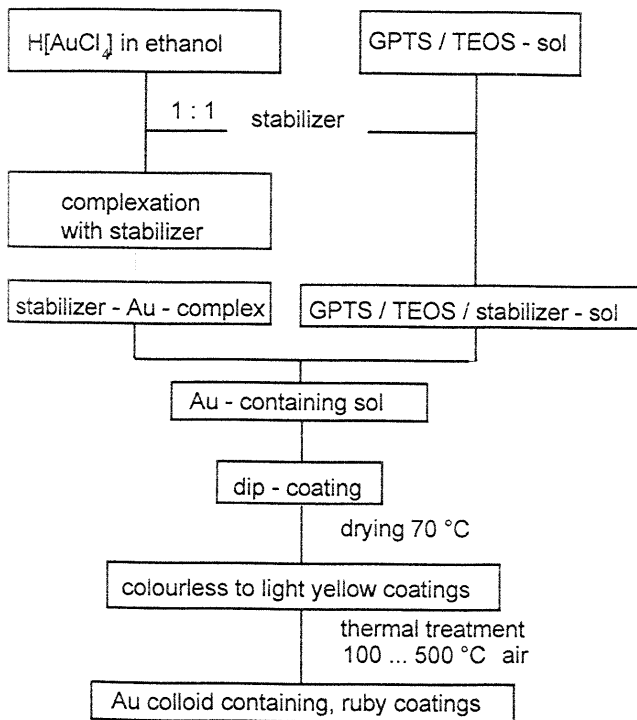


Fig. 1: Flow chart for the preparation of Au colloid containing coatings

The aim of the paper was to study the influence of different types of silane ligands on the formation of gold colloids in SiO₂ coatings on glass and to get a deeper insight whether these ligands have an impact on the nonlinear optical properties of the gold colloids in the coatings. For this reason it was decided to synthesize the Au colloids in a dense organic-inorganic matrix at relatively low temperatures and then to burn off all the organics, including the silane ligands and to compare the nlo properties for both cases. For this purpose the GPTS/TEOS system was chosen, since it is known from other investigations^{2, 7}, that its short chained organic groups can be completely burnt off without cracking or discolouring coatings of about 1 μm in thickness. As a precursor for Au H[AuCl₄]₃H₂O was used, since it is well soluble in organic solvents and does not contain additional cations that might disturb the formation of the SiO₂ network in the coating. According to Pearson's theory of soft and hard bases¹² two different types of ligands are chosen, to examine the dependence on the particles growth and nonlinear optical properties.

Thiosilane is a soft base and the amino groups are hard bases with respect to the Au³⁺-Ions. Fig. 1 shows a flow chart of the coating preparation. Concentrated solutions of H[AuCl₄]₃H₂O in ethanol are yellow and show a charge transfer absorbance band at 320 nm wavelength⁹. But they are unstable and Au colloid formation is obtained at room temperature. After adding aminosilanes APTS, DIAMO or TRIAMO in an equimolar ratio to Au clear, deep orange solutions were obtained. In the case of THIO the solutions were

colourless. The colour change points out a change of the Au-chloro-complex and one may assume that the Cl⁻ ions are replaced by the silanes successively as it is known for the bipyridin complex

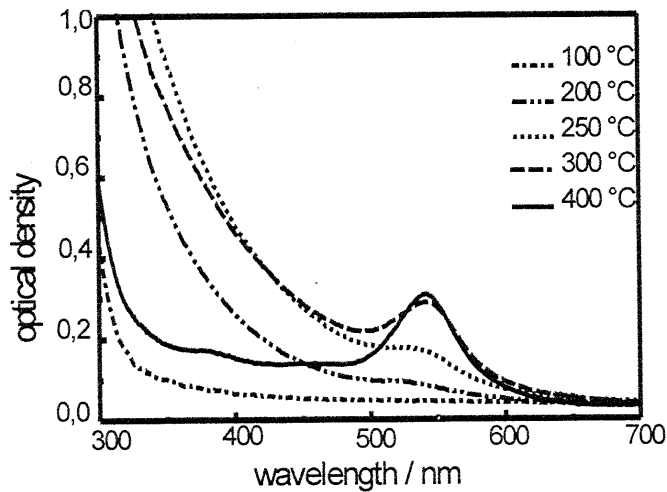


Fig. 2: Absorbance spectra of Au-containing GPTS/TEOS coatings on glass synthesized with DIAMO (Au : DIAMO1 :20) after thermal densification at different temperatures (reference: air)

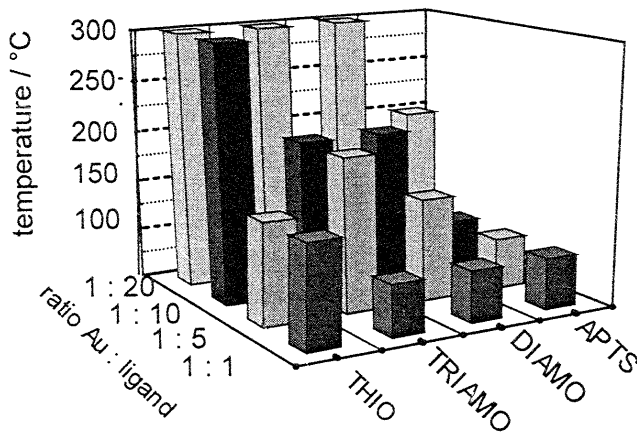


Fig. 3: Onset temperature of Au colloid formation in GPTS/TEOS coatings on glass for different kinds and concentrations of stabilizers.

[AuCl₂(bipy)]AuCl₄ that absorbs in the range between 375 and 550 nm wavelength¹⁰. A more precise discussion of the different Au complexes requires further investigations which is not the subject of this paper. When the amino silanes were added in ratios higher than 1:1 deep orange precipitations were obtained. In order to realize higher amounts of amino silanes in the coating sols the excess of them was added first to the prehydrolysed GPTS/TEOS sol and than mixed with the Au containing solutions. In this way clear sols could be prepared that did not show any spontaneous Au colloid formation during 24 days at room temperature or after drying appropriate coatings at 70 to 80 °C. During the further thermal treatment of the coatings the formation of Au colloids was monitored by UV-VIS spectroscopy as shown in fig. 2 for the example of DIAMO with a molar ratio to Au of 20 : 1. It can be seen that after drying at 100 °C no Au colloids can be detected in the spectrum but already after thermal treatment at 200 °C a slight absorbance occurs at about 530 nm that increases to the well known surface plasmon absorbance band of Au colloids with increasing temperature. Simultaneously a strong absorbance in the UV range is observed after 200 °C that may be attributed to decomposed organics in the coating. It increases at 250 °C, slightly decreases after 300 °C and completely vanishes after thermal treatment at 400 °C (the residual absorbance in the wavelength range below 500 nm is assumed to be due to intraband excitations of the Au-particles). Thickness

measurements of the coatings show almost constant values after densification between 100 and 300 °C, a shrinkage from 1.0 .. 1.2 µm to approx. 0.5 µm after treatment at 400 °C and no further decrease after 500 °C. Therefore it can be concluded that the major organic content of the coatings is burnt off after thermal treatment at 400 °C. In order to illustrate the influence of the kind and the concentration of the stabilizing silanes on the Au colloid formation the temperature for the onset of the Au colloid formation was determined from the UV/VIS spectra. The densification temperature was varied in 50 K steps and after subtracting the absorbance spectrum of an Au free reference sample the onset temperature was defined as the temperature where the plasmon resonance and intraband excitations could be detected for the first time.

The result is summarized in fig. 3. It shows that the colloid formation requires higher temperatures for the amino silanes with higher contents of amino groups per silane molecule with the exception for the Au to ligand ratio of 1 : 1. For each type of amino silane the formation temperature also increases with increasing silane concentration. It has to be assumed that with a ratio of 1 : 1 the different ligands do not affect the formation temperature of the colloids because the degree of complexation of the Au is low. The higher ratios show the tendency to an increase of the formation temperature. This is also affected by the number of amino groups per silane molecule. With increasing number of amino groups in the silane a chelat complex formation is favoured more and more and thus more stable complexes are formed by DIAMO or TRIAMO compared to APTS. Following Pearson's concept of hard and weak acids and bases Au^{3+} belongs to the weak Lewis acids¹¹ and therefore should form more stable complexes with soft bases as for instance the thiosilane than with hard bases (aminosilanes). This is clearly seen in fig. 3 for a silane to Au ratio of 1 : 1. The colloid formation temperature is higher in the case of thiosilane than for the aminosilanes. With higher silane concentrations higher temperatures are required and a difference between thio- and aminosilane not found experimentally. For a precise interpretation the complexes have to be studied more in detail and one should take into account that the aminosilanes and the thiosilane show different interactions with the sol-gel matrix. Aminosilanes may catalyse the SiO_2 network formation and

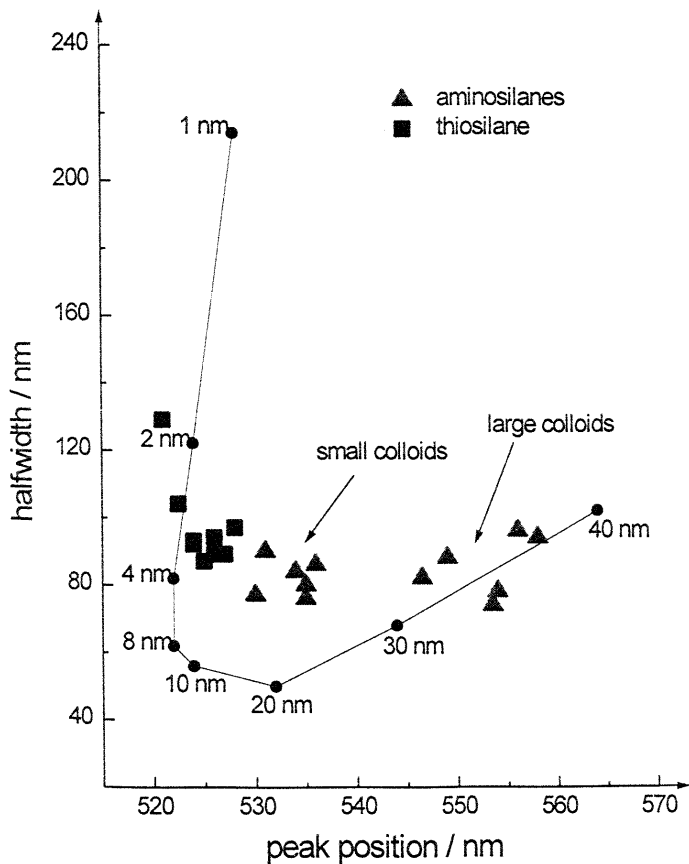


Fig. 4: Halfwidth and peak positions of calculated (Mie theory) extinction bands of Au colloids for different radii in a dielectric matrix (refractive index of 1.52) and values from measured absorbance curves

this could lead to a reduced mobility of Au-ions compared to the thiosilane at elevated temperatures. The next question to answer was, how the different stabilizers influence the size of the Au colloids. For this purpose extinction spectra were calculated according to the Mie theory following a formalism described in¹². A computer calculation programme was used¹³, which considers the mean free path effect of the conduction electrons in small particles as well as the contribution of the valence electrons to the dielectric function of Au. The peak positions (λ_{max}) and the halfwidth ($\Delta\lambda$) of extinction bands, calculated for different colloid radii were determined graphically and plotted in the parameter diagram shown in fig. 4. The curve shows that the extinction band is narrowing with increasing colloid size until $\Delta\lambda$ reaches a minimum in the range of 10 to 20 nm radius and then increases again with further increasing particle sizes. The peak position remains almost constant for small particles and shifts to longer wavelenghtes for $R > 20$ nm. Such large particles cause scattering effects (livery gold ruby glass). Measured couples of $\Delta\lambda$ and λ_{max} excellently fit to the appropriate calculated curve in the case of Au

colloids in melted lead crystal glass¹². But fig. 4 shows some significant misfits especially in the case of small colloids synthesized with aminosilanes. For thiosilane the measured values of $\Delta\lambda$ and λ_{\max} are in relatively good agreement with the theory. Small colloids, synthesized with relatively high amounts of aminosilanes (see also next chapter) show a shift of the peak of about 10 nm to longer wavelengths. Although these couples of values for $\Delta\lambda$ and λ_{\max} are just in the middle between the two branches of the calculated curve in fig. 4 the colloids can be identified to be small since scattering does not occur. A long wavelength shift of the extinction band is obtained when the spherical shape of the colloids is distorted, but in this case the halfwidth is also increased significantly³. But since the colloid radii determined from the halfwidth of the measured absorbance curves in fig. 4 were in very good agreement with crystallite radii (4 ... 6 nm) obtained from WAXS measurements of the same samples, shape distortions can be excluded in a first approximation. A shift of the absorbance band to longer wavelengths without influence on the halfwidth can be realized, when the refractive index in the interfacial surrounding of the colloids is larger than the average value of the matrix, used for the calculation of the spectra. Calculations show that for the obtained 10 nm shift a refractive index of about 1.6 is required. This is a relatively low difference to the average value of 1.52, determined by ellipsometry and thus it is hypothesized that the use of aminosilanes leads to a modified interfacial region compared to thiosilanes. Using the results obtained in fig. 4 the radii of the Au colloids were determined and fig. 5 summarizes the result for a densification temperature of 500 °C. For Au : silane ratios of 1 : 1 the colloid formation starts at relatively low temperatures (see fig. 3) during the slow thermal densification (1 K/min) of the composite and the final colloid size after 1 h at 500 °C decreases with increasing strength of the appropriate complex. For Au : silane ratios of 1 : 5 and 1 : 10 remarkable differences between the different stabilizers are not detectable. For an Au : stabilizer ratio of 1 : 20 the colloid formation starts at temperatures of about 300 °C, and in the case of DIAMO and TRIAMO very large particles are obtained in contrast to APTS and THIO. This is not understood yet, but it seems reasonable that the strength and extend of different Au complexes has a strong impact on the kinetics of nucleation and growth of the colloids. On the other hand it has to be taken into account that the different types of silanes influence the densification of the sol-gel matrix in different ways (e.g. enhanced densification, creation of pores during thermal decomposition of organics) and this may have an impact on the diffusion of Au-ions or atoms or on agglomeration or Oswald ripening of the colloids.

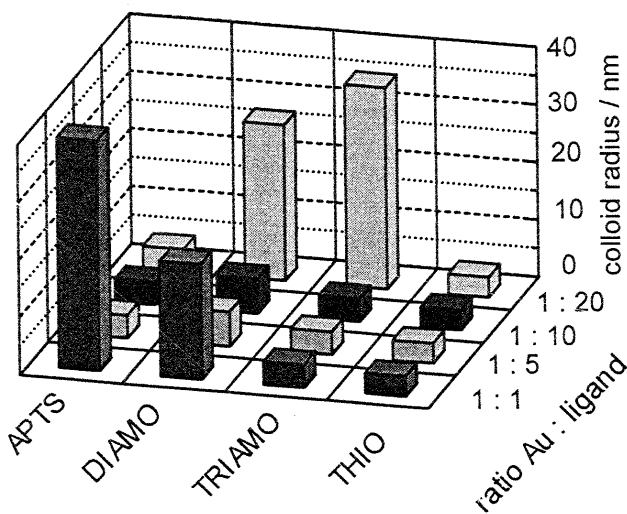


Fig. 5: Radii of Au colloids in GPTS/TEOS coatings on glass after thermal densification at 500 °C, determined from absorbance spectra

an impact on the diffusion of Au-ions or atoms or on agglomeration or Oswald ripening of the colloids.

3.2. NONLINEAR OPTICAL PROPERTIES

In order to compare the nonlinear optical properties of Au colloids synthesized with different kinds of functionalized silanes, samples with an Au : stabilizer ratio of 1 : 10 were chosen to ensure that colloid size effects are small (compare fig. 5). Samples treated with two different heating temperatures, namely 300 °C and 500 °C were measured to gain information about the matrix/colloid interface as already discussed in the

previous section. The colloid size of the samples treated at 300 °C is deduced from absorbance spectra and it was found no significant difference to the samples treated at 500 °C.

The $\chi^{(3)}$ values for the gold colloid containing coatings were calculated from the measured values of the diffraction efficiency η with equation (1)¹⁴. η is the intensity relation of the transmitted first and zeroth order of the diffraction pattern, which appears by selfdiffraction of a laser induced grating.

$$\chi^{(3)} = \frac{8 n^2 c^2 \varepsilon_0 \alpha \sqrt{\eta}}{3 \omega I_p (1 - T) \sqrt{T}} \quad (1)$$

n = refractive index
 α = linear absorption
 I_p = pump intensity

c = velocity of light
 ω = frequency of I_p
 T = transmission of I_p

These values are valid for the composit. To evaluate the third order nonlinear susceptibility in the gold particles, $\chi_m^{(3)}$, equation (2) and (3) are used¹⁵:

$$\chi^{(3)} = p f_1^2 |f_1|^2 \chi_m^{(3)} \quad (2)$$

$$f_1 = f_1(\omega) = \frac{3\varepsilon_d}{\varepsilon_m(\omega) + 2\varepsilon_d} \quad (3)$$

where p is the concentration of the Au particles, f_1 is the local field factor, ε_m is the dielectric function of the Au and ε_d the dielectric constant of the matrix. All samples except the one with thiosilane ligands are measured in the maximum of the Au colloid surface plasmon resonance. Because of wavelength restrictions due to the laser dye the samples with thiosilane ligands are measured on the low energy side of the resonance 2 nm far from the maximum and it is assumed that this slight deviation has no significant influence on the obtained nlo properties. To get a complete characterization of the composit all material parameters needed in equations (1) ... (3), namely particle concentration, the dielectric constants of the Au and the matrices at the excitation wavelength are measured and used for calculation. Since all parameters in the local field factor f_1 have an influence on the $\chi_m^{(3)}$ (f_1 is in the fourth power) the size dependence of the dielectric function of the Au colloids was taken into account too and ε_2 of the Au particles was determined by FWHM (full width at half maximum) of the plasmon resonance via the relation (4)¹⁵:

$$\frac{w}{w_\infty} = \frac{\varepsilon_m''}{\varepsilon_m''^\infty} \quad (4)$$

where w = FWHM of the plasmon resonance with $w_\infty \cong 60$ nm and $\varepsilon_m''^\infty = 2.4$ for the values in the large particle limit¹⁶. The volume fraction p of the Au colloid content is extracted from the absorption spectra by equation (5)¹⁵:

$$\alpha = p \frac{\omega}{n_d c} |f_1|^2 \varepsilon_m'' \quad \text{with } n_d = \text{refractive index of the matrix.} \quad (5)$$

To prove that the signal is really due to a third order nonlinear effect the quadratic dependence of the grating efficiency was measured versus pump intensity, and, as shown in fig 6, the curves show the slope of 2 in a very good approximation. With excitation intensities larger than 1 MW/cm² the samples with APTS- and DIAMO stabilized particles (heating temperature = 300 °C) exhibit saturation in the grating efficiency, which is reversible. Material distortions are not obtained by these high excitation intensities. The material parameters and the $\chi^{(3)}$ and $\chi_m^{(3)}$ values are listed in table 1. Table 1 shows the influence of the heat

treatment on the material parameters very clearly. The maximum absorption and the particle concentration are increased after densification at 500 °C due to the shrinkage of the composite coatings, whereas the refractive index n_d is lowered caused by the further removal of the organics. The peak positions and the and the FWHM keep unchanged, indicating that no significant particle growth has taken place.

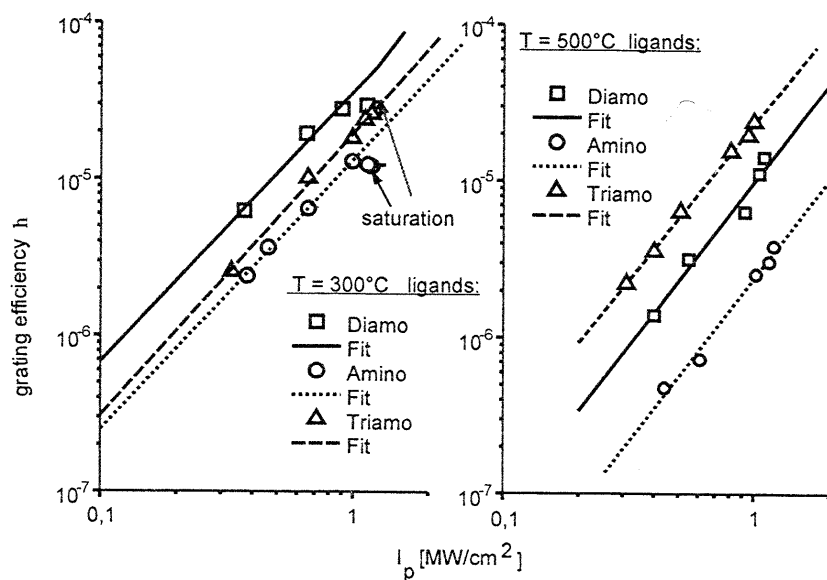


Fig. 6: grating efficiency η versus pump intensity

The $\chi^{(3)}$ and $\chi_m^{(3)}$ values are calculated with these parameters including estimated experimental errors, probably caused by laser intensity fluctuations and local variations of the thickness of the coatings. The $\chi^{(3)}$ values of all sol-gel composites prepared with aminosilanes are three to four orders of magnitude higher than comparable results in melted glasses¹⁵ and one order larger than obtained in sapphire¹⁷. But the samples synthesized with mercaptosilane show only a weak fluctuating signal at high excitation intensities which did not allow a serious evaluation of $\chi^{(3)}$. The measured values are in the same

range as the results obtained in ion implanted glasses¹⁸. Since particle size effects can be excluded in first approximation and the concentration of Au colloids is comparable to the coatings synthesized with aminosilanes, it has to be concluded that the large differences in the $\chi^{(3)}$ values between the samples derived from aminosilanes and thiosilane are attributed to interfacial influences of the ligands. One would expect that influences of the different types of ligands should be eliminated after densification at 500 °C, since the organics are burnt off at this stage. But this is not obtained, since the $\chi^{(3)}$ values of the samples prepared with aminosilanes are still much larger than those for the samples derived from thiosilane. In order to get an approach to this surprising effect, the $\chi_m^{(3)}$ values shall be discussed.

The calculation of the $\chi_m^{(3)}$ reveals values up to more than two orders of magnitude higher than in Au containing glass ($2.8 \cdot 10^{-8}$ esu)¹⁵. These values are comparable to other sol-gel prepared samples^{3,6}. A comparison of the $\chi_m^{(3)}$ values obtained for the different types of ligands after densification at 300 °C and 500 °C shows, that after the thermal treatment at 500 °C the $\chi_m^{(3)}$ values are almost equalized for the aminosilanes remaining much larger than in the case of the thiosilane. It is hypothesized that this surprising effect may be attributed to specific influences of the different types of silanes on the densification of the interfacial region of the Au colloids in the matrix, since from the linear optical properties it could be assumed (compare fig. 3), that thiosilane leads to „naked“ Au colloids compared to aminosilanes, that yield to an interfacial region with increased refractive index. This would enhance the local field factor f_1 (compare equation (3)) in the interfacial region of the colloids and therefore the calculation of the $\chi_m^{(3)}$ using equation (2) leads to high values, since here the lower average value of the dielectric constant of the dielectric matrix (ϵ_d) was used in equation (3). Distortions of the spherical shape of the colloids are assumed to be another reason for an enhanced local field factor⁵. From the linear optical properties (compare fig. 3) as well as from first electron

microscopical investigations it is concluded that using high surplus amounts of stabilizing ligands leads to spherical particles, but this has to be investigated in future experiments more in detail.

Table 1: determined parameters used for calculation of $\chi^{(3)}$ and $\chi_m^{(3)}$: The values in the brackets are the maximum experimental errors.

ligand	absorption	refractive index n_d	peak-max.	FWHM	ϵ_2 [15]	p	$\chi^{(3)}$	$\chi_m^{(3)}$
	α [m^{-1}]		λ [nm]	[nm]		[Vol. %]	[esu]	[esu]
heating temperature = 300°C								
APTS	$1,64 \cdot 10^5$	1,51	535	76	3,04	1,39	$9,6 \cdot 10^{-9}$ ($\pm 1,4 \cdot 10^{-9}$)	$3,0 \cdot 10^{-7}$ ($\pm 4,8 \cdot 10^{-8}$)
DIAMO	$3,08 \cdot 10^5$	1,55	532	90	3,60	2,80	$6,3 \cdot 10^{-8}$ ($\pm 9,4 \cdot 10^{-9}$)	$1,4 \cdot 10^{-6}$ ($\pm 2,2 \cdot 10^{-7}$)
TRIAMO	$3,29 \cdot 10^5$	1,53	536	86	3,44	3,02	$2,9 \cdot 10^{-8}$ ($\pm 4,3 \cdot 10^{-9}$)	$5,6 \cdot 10^{-7}$ ($\pm 8,9 \cdot 10^{-8}$)
Thiosilane	$1,90 \cdot 10^5$	1,53	522	104	4,16	2,06	-	-
heating temperature = 500°C								
APTS	$4,93 \cdot 10^5$	1,46	535	84	3,36	5,86	$2,5 \cdot 10^{-8}$ ($\pm 3,8 \cdot 10^{-9}$)	$3,4 \cdot 10^{-7}$ ($\pm 5,4 \cdot 10^{-8}$)
DIAMO	$4,92 \cdot 10^5$	1,48	532	77	3,08	4,45	$6,3 \cdot 10^{-8}$ ($\pm 9,5 \cdot 10^{-9}$)	$7,0 \cdot 10^{-7}$ ($\pm 1,1 \cdot 10^{-7}$)
TRIAMO	$5,51 \cdot 10^5$	1,47	535	80	3,20	5,55	$6,0 \cdot 10^{-8}$ ($\pm 9,0 \cdot 10^{-9}$)	$6,9 \cdot 10^{-7}$ ($\pm 1,1 \cdot 10^{-7}$)
Thiosilane	$4,31 \cdot 10^5$	1,49	524	92	3,68	4,47	-	-
ref. [3]: Au:DIAMO 1:1, UV-curing, + thermal treatment (200°C)								
Diamo	$3,81 \cdot 10^5$	1,52	539	60	2,4	2,3	$2,8 \cdot 10^{-7}$ ($\pm 4,2 \cdot 10^{-8}$)	$2,0 \cdot 10^{-6}$ ($\pm 3,1 \cdot 10^{-7}$)

The thermal treatment at 500 °C leads to a significant decrease of the $\chi_m^{(3)}$ value for the sample, synthesized with DIAMO. After densification at 300 °C its $\chi_m^{(3)}$ value is almost equal to that obtained in an Ormocer coating³, prepared with an Au : DIAMO ratio of only 1 : 1 using a combined UV- and thermal curing process with a maximum temperature of about 200 °C (see last line in table 1). A final explanation cannot be given at this stage of investigations. Structural parameters have to be investigated more closely.

The origin of the nonlinearity in the Au particles is well known. The interband contribution which has a negative sign in the nonlinearity with an estimated value of approx. $\text{Im}\{\chi^{(3)}\} \approx -1.7 \cdot 10^{-8}$ esu and the hot electron contribution with a positive change of $1.0 \cdot 10^{-7}$ esu are assumed¹⁵ to be the main contributions to the large $\chi^{(3)}$ values of Au colloids in glass matrices. Since the used DFWM technique is not sensitive to the sign of the nonlinearity, time resolved measurements have to be performed to analyse the contributions of the electronic system of the particles and the matrix / colloid interface, because the relaxation time of the hot electrons into a thermal equilibrium with the nanoscaled lattice is in the ps scale and the excitation time in

this experiments is 20 ns. Nevertheless a large contribution which origins from hot electrons in thermal equilibrium with the lattice is reported too [lit. cited in 15]. Further experiments with z-scan technique are under investigation to evaluate the sign of the nonlinearity.

4. CONCLUSION

The investigations have shown that the growth of Au colloids in sol-gel derived glass like coatings can be controlled in a relatively wide range using different types and concentrations of functionalized silanes for the sol synthesis. The compatibility of the matrix material, synthesized from a prehydrolysed GPTS/TEOS sol is assumed to be a decisive requirement for this synthesis route that leads to crackfree and transparent inorganic coatings after thermal densification at 500 °C. If aminosilanes are used in the sol synthesis Au colloids with relatively large $\chi_m^{(3)}$ values between 3 to $7 \cdot 10^{-7}$ esu are obtained, even after the organics have been burnt off. Since coatings with comparable material parameters, synthesized with a thiosilane show nonlinear coefficients that are much smaller, the main conclusion is drawn, that the silanes influence the interface between the Au colloids and the matrix and that this may be the key for the tailoring of optical nano composite materials with enhanced nonlinear optical susceptibilities.

For the explanation of the basic physical effects in these materials, time resolved measurements have to be carried out in the future.

5. ACKNOWLEDGEMENT

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