4.1.1 COLORED COATINGS ON GLASS BASED ON NOBLE METAL COLLOIDS

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1. INTRODUCTION

It is known from the Drude theory [1] that the color shown by nano-sized metal particles in a dielectric matrix is due to a surface plasmon resonance effect of the conductive electrons, which leads to a selective absorbance in the visible spectrum. The molar coefficient of the absorbance is in the range of 10^5 to 10^6 l/mole cm, which makes metal colloids very interesting and efficient dyes to obtain colored sol-gel coatings with thickness around 1 µm. Furthermore their extremely high UV and thermal stability are favorable for practical applications.

An excellent overview on the optical properties of metal colloids embedded in dielectric media was given by Kreibig and Vollmer [2]. For diluted systems, the absorbance coefficient k can be calculated according to the Mie theory [3] using equation (1)

$$k = \frac{6 \cdot \pi \cdot n_d \cdot NV}{\lambda} \cdot \mathrm{Im}\left\{ \sum_{\nu=1}^{\infty} a_\nu + p_\nu \right\} \qquad (1)$$

where NV denotes the volume concentration of the particles, n_d the refractive index of the non absorbing dielectric matrix and λ the wavelength of light in vacuum. a_ν and p_ν represent the contributions of the electric and magnetic partial waves, which can be calculated as a function of λ, n_d and the real (ε_{1m}) and imaginary part (ε_{2m}) of the dielectric function of the metal particles. Kreibig et al had shown [4,5] that, due to the small size of the metallic nanoparticles, additional collisions of the electrons occur at the particle walls. This „mean free path effect“ leads to an increase of the collision frequency of the electrons which is taken into account by adding a term v_F/R (v_F = Fermi velocity, R = radius) and which gives therefore particle size dependent expressions for ε_{1m} and ε_{2m}. The absorbance k as a function of λ, n_d, NV, ε_{1m} (R) and ε_{2m} (R) can be calculated using numeric methods [6-8].

The absorbance band of the colloids is characterized by the spectral position of the plasmon peak λ_{max}, the height of the peak (k_{max}) and the half band width $\Delta\lambda$ (figure 1 left). The results of theoretical and experimental investigations with Ag [9,10] and Au colloids [7] in glass are summarized in figure 1.

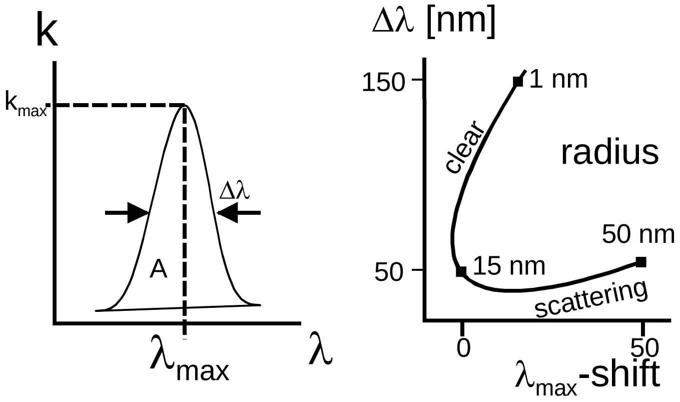

Figure 1. Characterization of the absorption band (left) and dependence of the peak position shift and half band width of the absorption bands of Ag and Au colloids in glass with their radius [from 7, 9, 10] (right).

For small particles with radii of up to approximately 15 to 20 nm, the half band width strongly decreases with increasing particle size, whereas the peak position of the absorbance band remains almost unchanged. Appropriate glasses appear clear and transparent, since scattering can be neglected for such small particles and the absorbance is due to absorption only. Increasing further the particle size, the half band width starts to increase and the peak shifts slightly to longer wavelengths. Here scattering becomes more and more evident and appropriate composites appear translucent. The parameter diagram of Figure 1 can be used to determine the average colloid size from spectroscopic data, since it has been shown by several investigations on Ag [9-11] and Au colloids [7,12] that the measured values of $\Delta\lambda$ and λ_{max} are in good agreement with the theoretical curve of figure 1.

Furthermore, the area beneath the absorbance curve was found proportional to the volume concentration of the metallic colloids [10]. The proportionality factor depends only slightly on the particle size [10,13], but depends on the refractive index of the matrix. These theoretical and experimental investigations lead to the conclusion that for a given matrix, the color seen in transmission obtained with metal colloids strongly depends on the type of metal and cannot be changed significantly by the particle size, when scattering is excluded.

However, as mentioned above, the color of a metal colloid composite system does not only depend on the type of the metal, but also on the refractive index of the matrix (equation 1). In order to illustrate this influence, the absorbance spectra of Ag colloids have been calculated numerically [8] for matrices with refractive indices varying from 1.3 (water) to 2.7 (TiO_2, rutile). Figure 2 shows that the absorbance of 10 nm Ag colloids is shifted to longer wavelengths and that the height of the absorbance increases significantly with increasing refractive index of the matrix ($1.3 < n < 2.7$).

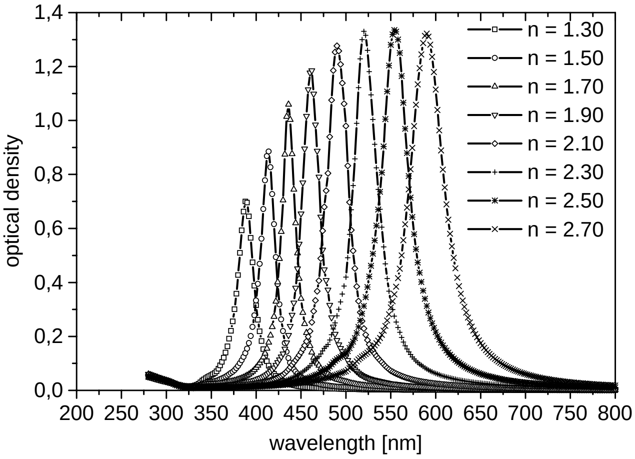

Figure 2. Calculated absorbance spectra of Ag colloids (10 nm radius, 10^{-6} vol.%) imbedded in dielectric matrices (thickness 1 mm) of different refractive index [8].

2. STATE OF THE ART FOR METAL COLLOID CONTAINING COATINGS ON GLASS

Au colloids have been generated in sol-gel derived SiO_2 coatings deposited on glass using a sol made by dissolving $AuHCl_4$ in tetraethoxysilane (TEOS) [14-16] or by incorporating appropriate precursors in ormosil matrices [17]. There have been also a few attempts to generate Ag colloids in SiO_2 matrices by dissolving $AgNO_3$ in sols prepared from TEOS [18] or tetramethoxysilane [19], using different reducing agents like formaldehyde [18] or Sn^{2+} [19] or by adding an aqueous colloidal Ag solution to a TEOS sol [20]. In a similar manner, Au colloids have been prepared in TiO_2 coatings on silica [21,16]. The common problem of these approaches is that the mechanisms for the control of the colloid size is still unknown. From the rather broad absorbance spectra and from TEM pictures it was concluded that the size distributions of the colloids were broad and that agglomeration could not be avoided completely.

However it is known that the agglomeration of metal colloids in solutions and polymers can be avoided by stabilizing these colloids with surface ligands, leading to a minimum of the Gibbs free energy of the system. Henglein [22-24] described the generation of colloidal metal and semiconductor nanoparticles (e.g. HgS, Ag_3S-CdS, PbS, Ag, Au, Pd) in alcoholic solutions by wet chemical or photochemical (photolytical decomposition of acetone) reactions of appropriate organometallic complexes. The stabilization of the colloidal particles was obtained by organic surface ligands, used as complex forming agents for the noble metal ions before to initiate the nucleation and growth reactions. Schmid [25,26] prepared Au, Pt and Pd colloids and bimetallic colloids (Au/Pt, Au/Pd, Pd/Pt) by dissolving appropriate metal salts such as H_2PdCl_4, H_2PtCl_6 or $HAuCl_4$ in water and by redox reactions with citrates. For the stabilization of the colloids, phosphoric salts ($P(m\text{-}C_6H_4SO_3Na)_3$, $P\text{-}H_2N\text{-}C_6H_4SO_3Na$) were used. Bönnemann et al. [27,28] have described an elegant way for the preparation of noble metal colloids, stabilized with tetra alkyl amines, by reduction and simultaneous stabilization of the noble metal salts with tetra alkyl boronhydride.

For composite materials, metallic nanoparticles have been generated and stabilized in reverse micelles, polymers and zeolithes [29,30]. In [31,32] functionalized silanes are shown to be suitable for the stabilization of metal colloids (Au, Ag, Pd) in appropriate SiO_2 xerogel powders by densification in air and a second thermal treatment in H_2 gas atmosphere.

Based on this knowledge, new synthesis and processing routes have been developed to obtain Au colloids in organic-inorganic hybrid (Nanomer®) coatings on glass [33,34], Pd colloids in SiO_2 coatings [35] and organic-inorganic monoliths [36], Au [12], Cu [37] and Ag [38] in SiO_2 coatings and also in SiO_2 – PbO coatings [39,40].

The basic idea (for details see [12, 33-40] was to use functionalized silanes (aminosilanes) like 3-amino propyl triethoxy silane (APTS), N-(2-amino ethyl)-3-amino propyl trimethoxy silane (DIAMO), trimethoxy silyl propyl diethylentriamine (TRIAMO) or thiosilanes like 3-mercapto propyl trimethoxy silane THIO) for the stabilization of the noble metal ions to allow the formation of appropriate complexes in alcoholic solution and to add this to the coating sol, in order to avoid a spontaneous reduction and colloid formation in the sol or during the wet film preparation. Colloids are formed afterwards during the densification step of the matrix, which can be either an organic-inorganic hybrid (Nanomer®), a glass-like or a ceramic material.

State-of-the-art SiO_2 coating sols [41] like acid catalyzed TEOS sols cannot be used for the formation of metal colloids in glass-like SiO_2 and PbO-SiO_2 coatings as a rapid gelation occurs due to the pH increase obtained during the formation of metal-aminosilane or metal-thiosilane complexes. This problem was overcome by using sols prepared from 3-glycidoxypropyl triethoxysilane (GPTS) and TEOS [42]. Surprisingly, it was found that despite of the high organic content of this sol, clear, transparent and crack-free coatings with thicknesses up to 0.8 μm could be obtained on glass after firing at temperatures between 500 °C and 700 °C [42] even in N_2 and N_2/H_2 atmosphere.

The colloid formation occurs by nucleation and growth processes during the densification of the matrix while thermal decomposition of the organic residuals allows the reduction of the noble metal ions in the temperature range between 250 and 400 °C [12,38]. In addition, the colloid mobility in the coating matrix is decreased by the densification process of the surrounding matrix. These processes can be controlled by the processing parameters (temperature and time, reducing gas atmosphere) and also by the kind and concentration of the used stabilizer. This has been shown for Au colloids in SiO_2 [12], where average colloid sizes between 3 and about 30 nm have been obtained. This result is consistent with those obtained by SAXS measurements on Au colloids contained in SiO_2 coatings on glass as a function of densification temperature, which indicate a fuzzy colloid to matrix interface at intermediate temperatures around 300 °C [43,44].

The principle of stabilization of the metal ions in a sol was also successfully applied for the formation of Au, Ag and Pd colloids in TiO_2 and ZrO_2 coatings [45,46]. Again, the colloid formation occurs during the densification of the matrix where a reducing gas atmosphere had to be used for Ag and Pd. The TiO_2 or ZrO_2 matrix were synthesized from titanium or zirconium isoproxide using state-of-the-art synthesis routes [21].

3. APPLICATIONS

Based on these synthesis routes, transparent colored coatings have been developed for silicate prescription eye glass lenses [47] and for flat glass [48] on an industrial scale and for halogen lamps [48] on lab scale. Since the color range obtained with different metals in a given matrix is limited, mixtures of Ag and Au colloidal sols have been also developed in order to obtain amber, red and green colors [48].

Another possibility to extend the color range of metal colloid coatings on glass is the case of colloids in mixed oxide coatings. As an example, Figure 3 shows the absorption spectra of Ag colloids (9.3 mole-% Ag) imbedded in a SiO_2 coating, in a ZrO_2 coating and in mixed SiO_2/ZrO_2 coatings deposited on boron silicate glass after thermal densification at 500 °C in reducing atmosphere [46].

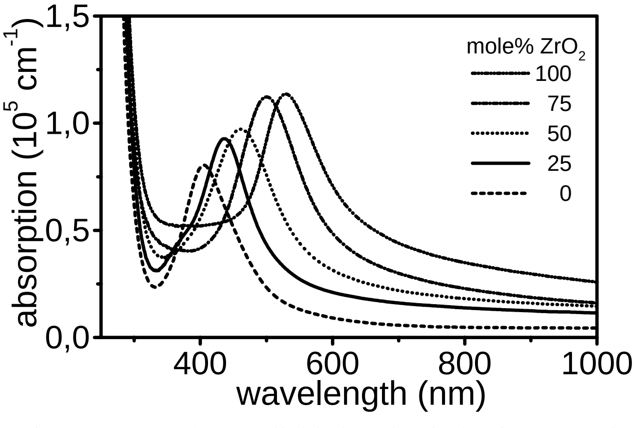

Figure 3. UV/VIS spectra of Ag colloids in mixed SiO_2/ZrO_2 coatings (double-

sided) of different molar ratios deposited on boron silicate glass after 1 h at 500 °C in reducing atmosphere (Ag content: 9.3 mol-%) [46].

The plasmon peak of the Ag colloids is red shifted from 405 nm (pure SiO2 matrix) to 535 nm (pure ZrO2) and are qualitatively in good agreement with the theoretical result (Figure 2).

The described decorative coatings show excellent adhesion on fused silica, boron silicate (Borofloat) and float glass. Different stability tests have been performed and no change in the absorbance spectra (difference in transmittance < 1 %) were obtained after 7 days at 300 °C, 10 days in a suntest equipment and 10 days in a climate test equipment. The scratch resistance of the coatings is the same as for silicate glass and therefore these coatings fulfill the general demand for the application of colored coatings on glass.

For an efficient industrial application of colored prescription eye glass lenses of various geometrics a technology has been even developed using a spin coating process allowing to obtain coatings of four different colors using only one matrix sol, one set of process parameters and a densification process for all the colors performed in the same furnace.

For the application on flat glass, flat spray technology [49] and flexoprinting [50] have been applied successfully. The coatings can also be applied by dipping, e.g. for applications on halogen bulbs [51].

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