Synthesis of nanocomposite thin films containing Ag-Au alloy colloids for wavelength tunability

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A chemical solution deposition route to synthesize silver-gold alloy colloids in thin films with diameters between 8–35 nm has been developed. Ag-Au alloy colloids were synthesized by the addition of silver ions to a polymer protected aqueous gold sol in presence of a seeding agent 'hydroxylamine hydrochloride,' followed by a heat-treatment under reducing atmosphere at temperatures ranging from 150–550°C. The resonance wavelength of Ag-Au alloy colloids exists between those of pure Ag (410 nm) and pure Au (525 nm) colloids, which can easily be controlled by selecting the molar ratio of Ag to Au. This allows the tunability of the absorption wavelength (hence the color) by using Ag-Au alloy colloids in thin films.

1. Introduction

The coloring of glasses is an ancient art, but compared to this a rather new field in science. Coloration of glasses by metal or non-metal ions was known to mankind some thousand of years ago in Egypt [1]. In this method of coloring, each batch of glass must be melted separately and the colors produced are generally diffuse and dull. Another rather modern alternative for the production of colored glasses is to coat them with a film containing nanosized metal colloids (i.e., Ag, Au, Cu and Pd) [2]. This method allows the generation of very intense colors due to plasmon resonance by a film as thin as 100 nm. Furthermore, this method does not necessitate melting a separate batch for each color. Besides colored coatings such noble metal colloids have also been explored for non-linear optical applications due to their opto-electric potential.

Chemical solution deposition is a relatively new route to coat thin films on different type of substrates. The synthesis of monometallic particles like, Pd [3], Cu [4], Ag [5] and Au [6] colloids in SiO_2 and $PbO-SiO_2$ coatings [7] and Ag and Au colloids in TiO_2 [8] coatings have been carried out by this route. It is also known [9] that the color due to colloidal particles is dependent on the dielectric constant of the particle, which in fact can be changed by alloying or mixing of the two metals with different dielectric constants. Therefore, it is challenging and of scientific interest to synthesize the nanoparticles formed by the alloying of two different metallic species, and to investigate their optical properties.

Several methods have been used for the preparation of bimetallic colloidal particles in solution, e.g., chemical reduction [10, 11] or UV photo reduction [12, 13]

of the mixed solution of two metal salts. These systems showed interesting optical properties, however, the synthesis of such bimetallic colloidal particles in thin films has not yet been studied. The present work is therefore aimed to synthesize thin films containing Ag-Au alloy colloids, to get colors intermediate to those obtained by monometallic silver and gold colloids and to tailor the optical properties in visible region.

2. Experimental
2.1. Synthesis of GPTS-TEOS matrix sol

To fabricate thin films, matrix sol was synthesized from 3-glycidoxypropyl trimethoysilane (GPTS) and tetraethoxysilane (TEOS). The GPTS/TEOS sol with molar ratio of 4:1 was synthesized by taking a mixture of 120 ml ethanol, 160 ml GPTS and 40 ml TEOS in a flask connected with a water condenser and heating arrangement. After heating at 80°C for 0.5 h, 28.5 ml of 0.1 molar HNO_3 solution was added dropwise to it within 3–4 minutes. This mixture was reacted for 24 h under the same conditions at 80°C, and finally 120 ml more ethanol was added to it. After reacting it for 0.5 h at 80°C, the resulting sol was cooled to room temperature.

2.2. Synthesis of aqueous gold sol

Colloidal gold particles were synthesized in an aqueous solution in order to synthesize thin films containing Ag-Au alloy colloids. For that, 1.0 g of polyvinylpyrrolidone K15 (PVP) was dissolved in 10.5 ml of water in which 0.34 g of hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$) was dissolved. This solution was heated at 80°C for 5 min, followed by the dropwise

addition of an aqueous solution of sodium citrate dihydrate (0.88 g in 2 ml of water) under vigorous stirring. Resulting solution was maintained at 80°C for 10 min followed by cooling to room temperature with constant stirring for 30 min.

2.3. Synthesis of silver containing sol

SiO_2 sol containing silver was synthesized separately by dissolving 0.400 g $AgNO_3$ in 14 ml of methanol, in which 1.04 ml of N-(2-Aminoethyl-3-aminopropyl) trimethoxy silane (DIAMO) was added dropwise (molar ratio of Ag:DIAMO = 1:2). After stirring for 10 min at 25°C, 25 ml of GPTS/TEOS sol (molar ratio of GPTS:TEOS = 4:1) was added to it. This solution was stirred for 4 h to get SiO_2 sol containing silver. Whereas to synthesize a PbO-SiO_2 sol containing silver, 0.5 g of $Pb(CH_3COO)_2$ was dissolved in 5.0 ml methanol and 0.34 ml DIAMO was added as a complexing agent (Pb:DIAM = 1:1). This lead containing methanolic solution was added dropwise to the silver containing SiO_2 sol. The resulting solution was stirred at 25°C for 4 h.

2.4. Synthesis of sol containing Ag and Au

To synthesize Ag-Au alloy colloids with the molar ratio of Ag:Au = 2:1 (for example), 2.5 ml of gold sol (section 2.2) was taken in a glass container, followed by the addition of methanolic solution of hydroxylamine hydrochloride (0.11 g in 2 ml methanol). After that 6.8 ml of silver containing sol (section 2.3) was added to it followed by the addition of 15 ml of GPTS-TEOS sol. The resulting solution was stirred for 4 h at 25°C to get a low viscosity precursor solution. Samples were prepared by coating the sodalime glass substrates (dimensions 10 cm × 2.5 cm × 0.1 cm) using a dip coating technique, with the lifting speed of 4 mm/s and dried at 80°C for 30 min. These dried samples were heat treated under reducing atmosphere ($N_2/H_2 = 92/8$) with the heating rate of 100 K/h at temperatures of 150 to 550°C.

2.5. Characterization techniques

To investigate the optical properties, ultraviolet-visible (UV-VIS) absorption spectra of the films coated on the glass substrates were recorded with an OMEGA 30 UV-VIS spectrometer (Bruins Instrument) in the wavelength range from 300 to 1000 nm. The thicknesses of the films were measured with a profilometer (diamond stylus, nanosurf). To obtain the information about crystalline phase and the size of nanocrystals, X-ray diffraction measurements were conducted on a Siemens automated diffractometer working at 40 kV and 35 mA, with a LiF monochromator and Cu Kα (1.5405 Å) radiation. The diffracted X-rays were collected by scanning between $2\theta = 20$–$60°$ in 0.04° steps. Microstructural characterization of these samples was carried out using a high-resolution transmission electron microscope (JEOL 200 CX).

3. Results and discussion

The aqueous solution containing colloidal gold was synthesized by reducing Au^{+3} with sodium citrate

dihydrate. The yellow color of the $AuCl_4^-$ anions disappeared immediately after the addition of sodium citrate, after 3 min the solution slowly became violet and then deepened to a wine red color. Polyvinylpyrrolidone (PVP) was chosen as a stabilizer for gold, due to its solubility in water. The ratio of gold to PVP was kept same as reported in literature [14]. If no stabilizer was added, the addition of the reducing agent led to a brown precipitate. It is assumed that this was due to the agglomeration of the colloidal particles. As it is known that to obtain mono dispersed monometallic particles, some protective agent such as polyvinylpyrrolidone [15, 16] has often been required to stop coagulation and protect the agglomeration of particles in solution.

The formation of gold colloids was confirmed by UV-VIS spectroscopy. The absorption spectra of the sols containing colloidal gold showed a maximum at 526 nm, which corresponds to the plasmon peak of gold colloids, and the TEM analysis confirmed the formation of gold colloids of radii 8–10 nm in solution [17]. The amount of sodium citrate dihydrate for the reduction of ionic gold into colloidal gold was optimized for a 100% colloid turnover.

Silver was added dropwise to the gold sol in presence of hydroxylamine hydrochloride (HAH), which is known to reduce Ag^+ onto the surface of colloidal gold particles [18]. Complexing of silver with DIAMO was necessary, otherwise the addition of silver into the gold sol containing HAH always led to the AgCl precipitate. PbO was incorporated in the silica matrix in order to get the dense coatings after firing at 500°C [19], resulting a decrease in the rate of reduction of silver into silver oxide on standing in air. Lead acetate was chosen as a precursor for lead due to its good solubility in alcohol.

Morris et al. [18] have grown silver on colloidal gold nuclei, in an aqueous solution using hydroxylamine hydrochloride, which is known to retard the formation of silver nuclei and to favor the growth of silver nuclei on existing gold particles. Kenneth et al. [20] have also shown that the hydroxylamine functions as a seed for the growth of Au nanoparticles in solution. Therefore, colloidal gold nanoparticles as synthesized above were used for the synthesis of alloy colloids and it was expected that the addition of hydroxylamine followed by silver ions would facilitate the growth of the silver shell on the existing gold nuclei. During the heat treatment at higher temperatures, diffusion of silver particles inside the gold will take place and the alloy colloids will be formed. This is shown schematically in Fig. 1.
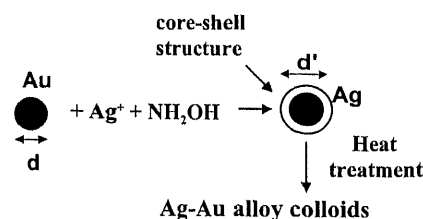

Figure 1 Proposed mechanism for the formation of Ag-Au alloy colloids.

Figure 3 The UV-VIS absorption spectra of PbO-SiO₂ thin films containing Ag-Au alloy colloids as a function of their molar ratios heat-treated at 350°C.
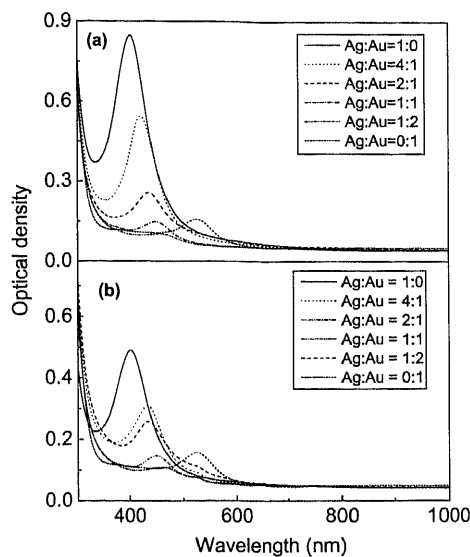
Figure 2 (a) UV-VIS absorption spectra of SiO₂ thin films containing Ag-Au alloy colloids, heat-treated at 350°C under reducing atmosphere (b) Absorption spectra after exposing the samples in air for 6 months.

3.1. UV-VIS spectroscopy

The UV-VIS spectra of Ag-Au alloy colloids in SiO₂ thin films as a function of their molar ratios at a constant densification temperature of 350°C are shown in Fig. 2a. This figure shows that plasmon peak always remains as a single peak and continuously shifts from 401 to 522 nm on increasing the molar fraction of gold. In a solution containing gold and silver ions two states are possible, (1) alloy particles and (2) particles with core-shell structure. The theoretical spectra calculated by Itakura et al. [21] for the core-shell type structure of Ag-Au, by using the equation given by Bohren and Hoffman [22] show that the single plasmon peak splits as two peaks, one of which is located at the shorter wavelength than that of silver plasmon peak and the other is located at the wavelength slightly shorter than that of gold plasmon peak. Whereas for the alloy colloids of gold and silver, the plasmon peak always remains a single peak. Therefore the particles formed under the present work are alloy colloids.

Exposing to atmosphere for longer times, the optical density of the absorption peak changed in these samples. Effect of 6 months exposure to air on UV-VIS spectra of the above samples is shown in Fig. 2b. On comparing Fig. 2a with Fig. 2b, it can be seen that for air exposed samples the peak intensities were decreased. This decrease in the intensity could be attributed to the oxidation of silver to silver oxide in air. The decrease in the peak intensities for the samples containing higher molar percentage of silver is large, whereas, for the sample containing pure gold no decrease in the intensity was observed. This is because the reduction potential for gold is higher that that of silver, hence gold will have lower tendency to oxidize in gold-oxide than the silver to silver-oxide. Besides that on standing the samples in air, a new absorption peak at 520 nm (characteristic plasmon peak of colloidal gold) was also visible. It indicates that reduced silver comes out from the alloy particles, leaving behind some monometallic colloidal gold particles.
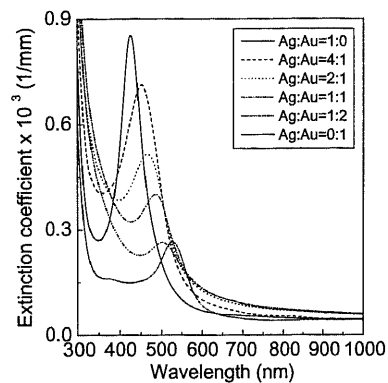
Lead oxide (PbO) is known to decrease the transformation temperature and to increase the thermal exponential coefficient of the glass when incorporated into SiO₂ [23] based glasses. The synthesis of PbO-SiO₂ thin films by the sol-gel route has been carried out by Strawbridge et al. [24] and James et al. [25]. M. Schmitt [19] has first made systematic investigations towards the synthesis of PbO-SiO₂ thin films containing silver and gold by the sol-gel route, in order to form dense coatings which could partially stop the penetration of oxygen from the atmosphere and hence the oxidation of the metal colloids. Therefore, Ag-Au alloy colloids were synthesized in PbO-SiO₂ thin films to avoid the oxidation of silver. The UV-VIS absorption spectra of PbO-SiO₂ thin films containing Ag-Au alloy colloids and densified at 350°C, are shown in Fig. 3 as a function of molar ratios.

It can be observed from the measured spectra of SiO₂ and PbO-SiO₂ thin films containing Ag-Au alloy colloids that the general trend of appearance of a single UV-VIS peak and a continuous shift from 401 nm to 522 nm with increasing molar ratio of gold is the same in both cases. But in case of PbO-SiO₂ coatings, the absorption peaks are located at longer wavelengths than in the SiO₂ coatings. This red shift can be attributed to the increase in the refractive index ($n_D = 1.50$) of the PbO-SiO₂ coatings.

The thicknesses of the PbO-SiO₂ and SiO₂ thin films were measured using a profilometer. For the SiO₂ films heat treated at 350°C the thickness was measured equal to 0.7 μm which decreases to 0.5 μm after heating to 450°C and finally to 0.3 μm after heat treating at 550°C. Whereas for the PbO-SiO₂ films, thickness was measured equal to 1.1 μm for the sample heat treated at 350°C, which decreases to 0.7 μm at 450°C and finally to 0.55 μm at 550°C.

3.2. Calculation of theoretical spectra of Ag-Au alloy colloids

In order to prove the hypothesis of the formation of Ag-Au alloy colloids, a computer simulation of the composition dependence of plasmon frequency was performed. As is known from the Mie's theory [26], the frequency of the absorption peak is proportional
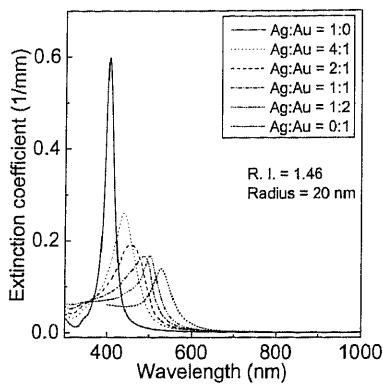
Figure 4 Theoretical extinction spectra for Ag-Au alloy colloids calculated after Mie-theory using a computer simulation programme (particle radius = 20 nm, refractive index of the matrix = 1.46).

Figure 5 Absorption spectra of thin films containing Ag-Au alloy colloids (Ag:Au = 2:1) densified at different temperatures.

to $\varepsilon_2/[(\varepsilon_1 + 2\varepsilon_0)^2 + \varepsilon_2^2]$, where ε_1 and ε_2 are the real and the imaginary parts of the dielectric constant of the metals and ε_0 is the dielectric constant of the medium. For calculating the absorption spectra of alloy colloids we take ε_1 and ε_2 to be the composition-weighted averages [27] of the bulk dielectric constants of Au and Ag (viz., $\varepsilon_i = (1 - x)\,\varepsilon_i{}^{Au} + x\varepsilon_i{}^{Ag}$ for $i = 1, 2$). Theoretical spectra obtained in this way for the alloy particles are shown in Fig. 4.

It can be seen from Fig. 4 that the plasmon peak remains as a single peak and continuously shifts from 410 to 530 nm with increasing molar fraction of gold. Comparing the observed (Fig. 3) and theoretical (Fig. 4) spectra it is clear that shifting of peak with increasing molar ratio of gold in the theoretical spectra is in good agreement with the observed spectra, the peak positions are however not same in both cases. It is assumed that this difference is largely due to, 1). The use of bulk dielectric constant for these nanosized colloidal particles is inappropriate, 2). Neglecting the effect caused by the smallness of the particle size compared with the electron mean free path [28].

The origin of the red shift in the case of Ag-Au alloy colloids is interesting. As silver and gold have identical bulk plasmon frequencies [29], a peak shift due to changing electron density is not expected. However, the high frequency dielectric constants are quite different, primarily because the interband transition in gold extends across most of the visible spectrum. So the absorption band shift in this case is due to the perturbation of d-band energy levels and not to changes in free electron concentration [29]. This results in a steady increase in the effective value of ε for the alloys and consequently, a red shift in the position of the absorption band.

The evolution of silver-gold alloy peak as a function of densification temperature for a constant molar ratio of Ag:Au = (2:1) is shown in Fig. 5. This figure shows that for the samples dried in air (20°C) a very broad band is observed, which is composed of two peaks, situated at 500 and 430 nm. On heating the sample up to 150°C the nature of the absorption peak remains same but there is a slight increase in the intensity of peak at 430 nm. While the sample heat treated at 250°C shows only one peak centered at 455 nm, which remains as
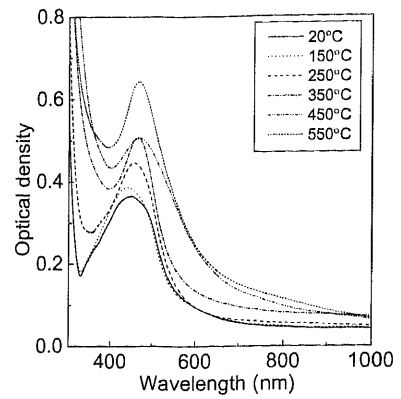
a single peak during the heat treatment at the higher temperatures up to 550°C.

Morris *et al.* [18] have measured the absorption spectra of silver coated gold particles in aqueous solution and have calculated the theoretical spectra using Adan and Kerker theory [30], for the different shell thicknesses. Starting with gold nuclei of 59 nm, concentric layers of silver ranging from 5 to 220 nm were deposited. They observed that as long as the silver shell thickness is less than 80 nm two peaks were obtained one due to gold, shifted slightly towards lower wavelengths and the other due to silver, which also shifted towards lower wavelengths. Whereas increasing the shell thickness to 100 nm gave only one absorption peak corresponding to silver and the gold peak was completely masked. Hence the absorption spectra obtained for the samples dried in air and heated up to 150°C may be attributed to a core-shell structure. Whereas, at higher temperatures the alloy formation takes place due to the diffusion of Ag into Au particles. Hodak *et al.* [31] have also made the same observation of conversion of core-shell structure to alloy colloids at elevated temperatures.

The UV-VIS absorption spectra of thin films as a function of increasing molar ratio of silver, hence the thickness of the shell at a constant densification temperature of 150°C can be seen in Fig. 6. It can be observed that for the molar ratio of Ag:Au = 1:2 and 1:1 two peaks located at 425 and 500 nm are visible. Whereas for the molar ratios of Ag:Au = 2:1 and 4:1, only one
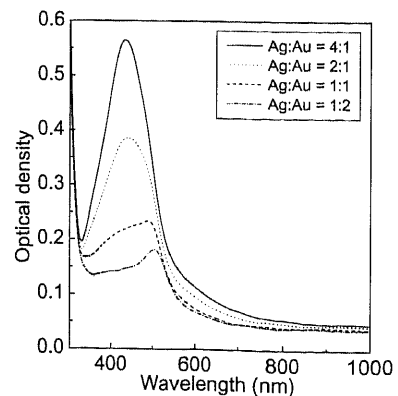

Figure 6 Measured absorption spectra of Ag-Au alloy colloids for different molar ratios, heat-treated at 150°C.

peak due to silver is visible which is centered at 430 nm, and the peak at 500 nm is completely masked. These observed spectra are in good agreement to the absorption spectra obtained by Morris *et al.* [18] for core-shell type particles of Ag-Au (with silver as a shell) in aqueous solution, except that the silver peak position observed in present study is slightly higher than that observed by them. This can be due to the increase in refractive index of the medium in the present case. Besides that an absorption spectrum corresponding to the physical addition of gold and silver mixed colloids was never obtained, it can be said that the particle in thin films are not phase separated particles of Ag and Au.

Baba *et al.* [32] have given a theoretical equation for Ag-Au alloy particles, which relates the absorption wave maxima of colloids with their molar fractions, in the following form, without using the dielectric constant of the individual particles.

$$1/\lambda_{\text{bimetallic}} = \left[\left(x_{Au}/\lambda_{Au}^2 \right) + (1 - x_{Au})/\lambda_{Ag}^2 \right]^{1/2}$$

Where λ_{Au} and x_{Au} are the maximum wavelength and the molar fractions for gold and λ_{Ag} and x_{Ag} are the maximum wavelength and the molar fractions for silver particles respectively. Wavelengths corresponding to maximum UV-VIS absorption from observed spectra and calculated wavelengths for alloy colloids using above equation are plotted against the molar fraction of gold. Fig. 7 shows the observed and calculated peak positions for alloy colloids in SiO_2 and PbO-SiO_2 matrices.

Here it is clear that the heating of the samples at higher temperature shifts the peak slightly towards lower wavelengths, i.e., for Ag:Au = 2:1, the absorption peak shifts from $\lambda_{max} = 437$ nm to $\lambda_{max} = 431$ nm on increasing the heat treatment temperature from 350°C to 550°C. This shift in the peak maxima could be explained by the fact that at higher temperatures more and more silver particles could diffuse inside the alloy particles, hence shifting the peak position towards the silver maximum was observed. The observed values for the peak maxima are in good agreement to the calculated ones. The same type of behavior was observed for the PbO-SiO$_2$ matrix also; here the deviation of the observed peak position from the calculated one is slightly higher than that for the SiO$_2$ glass. This slightly higher deviation in peak positions for the lead containing thin
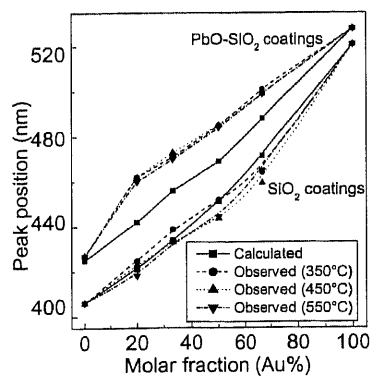
films can be attributed to the increase in the refractive index of the film by the addition of PbO. Refractive indices of the SiO$_2$ and PbO-SiO$_2$ thin films were measured 1.46 and 1.50 respectively by ellipsometery. The colloidal volume percentage for PbO-SiO$_2$ glass samples, heat treated at 550°C was calculated equal to 0.61% [17].

3.3. HR-TEM characterization of thin films containing Ag-Au alloy colloids

In order to determine the size and shape of the particles, high-resolution transmission electron microscopic (HR-TEM) studies were carried out. Whereas to examine the composition of the particles formed, EDX analysis of thin films containing Ag-Au alloy colloids was performed. Fig. 8a shows the Ag-Au alloy
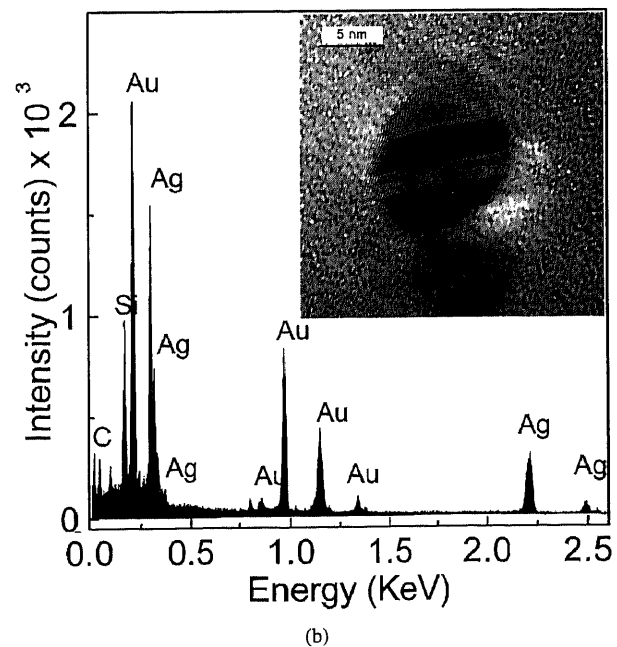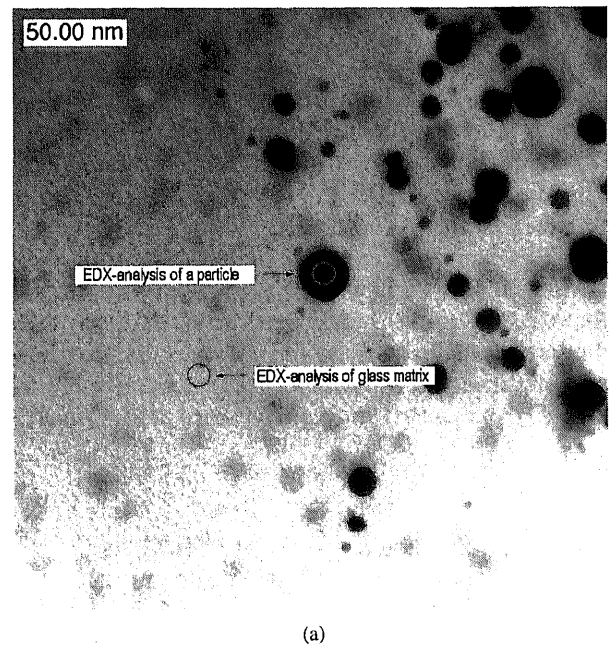

(a)

(b)

Figure 7 Measured and calculated (after Baba *et al.* [32]) peak positions of Ag-Au alloy colloids for different molar fractions of Au.

Figure 8 HR-TEM image of a sample containing Ag-Au alloy particles (Ag:Au = 4:1), (a) particle dispersed in glass matrix (b) high resolution micrograph and EDX spectrum of a single alloy particle.

particles dispersed in glass matrix. It can be observed that particles with diameters ranging from 8 to 35 nm were observed.

A lattice constant of 2.35 Å was determined from the above. Silver and gold are in fact miscible in all proportions due to almost identical lattice constants [33]. So the lattice plane spacing of 2.35 Å observed in HR-TEM may be attributed either to pure gold, pure silver or to silver-gold alloy. Thus the lattice plane spacing calculated for the individual colloidal particles does not differentiate between these possibilities. Therefore, electron dispersive X-ray analysis (EDX) of individual particles was carried out to estimate their composition, by focusing the electron beam on the individual particles. High-resolution image of a single Ag-Au alloy particle and its EDX profiles are shown in Fig. 8b.

This figure shows that this particular particle is composed of 81% (atom) of silver and 19% (atom) of gold, which is in good agreement with theoretical ratio of Ag:Au = 4:1. Analysis of several particles showed that the composition varies within ±10%, which could be because of experimental errors or it can be attributed to the variation of composition of different particles. The estimated results of 70% (atom) Ag and 30% (atom) Au for the molar ratio of Ag:Au = 2:1 and 33% (atom) Ag and 67% (atom) Au for the molar ratio of Ag:Au = 1:2 are in good agreement with the expected values. Therefore the EDX analysis of different particles shows that they are bimetallic particles and monometallic particles were not observed. However the EXD measurements on the SiO$_2$ glass matrix show the presence of Si, O and C only.

3.4. XRD characterization of thin films containing Ag-Au alloy colloids

In order to confirm the crystalline behavior and to determine the size of particles formed, XRD analysis of the samples containing bimetallic colloids of Ag and Au was carried out. The measured diffraction patterns for Ag-Au alloy colloids having molar ratios of Ag:Au = 4:1, 2:1, 1:1 and 1:2 are shown in Fig. 9. In all the cases the general behavior of the diffraction pattern is same, and four peaks are obtained. The peaks corresponding to $2\theta = 38.15°$ and $44.36°$ may be at-
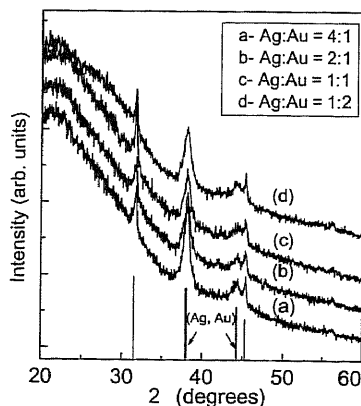
TABLE I Angle 2θ, corrected half width (β) corresponding to (111) peak and particle diameter 'd' after Scherrer equation for Ag-Au alloy colloids in PbO-SiO$_2$ glass coatings densified at 450°C

Ag:Au	2θ (°)	β (°)	'd' (nm)
4:1	38.067	0.771	15.7
2:1	38.091	0.783	15.4
1:1	38.100	0.864	13.5
1:2	38.098	0.880	13.5

tributed to gold-silver alloys. The two additional peaks corresponding to $2\theta = 31.70°$ and $45.48°$ are due to the presence of sodium chloride, which most probably was formed by the combination of sodium ion (from sodium citrate dihydrate) and chloride ions (from gold salt and hydroxylamine hydrochloride).

These X-ray diffraction patterns were used for the calculation of the crystallite size using the Scherrer equation. The most intense peak corresponding to gold-silver alloy colloids, which is centered at 38.15° was fitted with the cauchy profile and used for the particle size measurements. The particle size of Ag-Au alloy colloids, for the different molar ratios of gold and silver is shown in Table I. This table clearly shows that the particle size is almost same in all cases and is independent to the molar ratio of Ag and Au. The diameter of the crystallites calculated as above is in agreement to the particle size measured by HR-TEM in above sections.

4. Conclusions

In conclusion, a chemical solution deposition route for the synthesis of nanocomposite thin films containing Ag-Au alloy colloids has been developed successfully. Hydroxylamine hydrochloride has been shown to be an excellent seeding agent to grow silver onto the surface of pre-formed gold particles in solution; this core-shell structure can be retained in thin films up to 150°C. Structural and compositional analysis of Ag-Au alloy particles in silica matrix was performed by means of UV-VIS spectroscopy, HR-TEM and EDX. Thin films containing Ag-Au alloy colloids showed only one absorption peak the position of which can easily be controlled by changing the molar ratios of Ag to Au. This allows the tunability of the absorption wavelength (hence the color) by using alloy colloids in thin films. The theoretical absorption spectra for the alloy colloids of Ag-Au were calculated using Mie-theory and using an equation given by Baba et al. [32]. A good agreement was found between theoretical and measured absorption spectra of Ag-Au alloy colloids.

Figure 9 X-ray diffraction patterns of thin films containing Ag-Au alloy colloids.

The inset in the figure reads:
a- Ag:Au = 4:1
b- Ag:Au = 2:1
c- Ag:Au = 1:1
d- Ag:Au = 1:2

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