# SiO$_2$-coatings on glass containing copper colloids using the Sol-Gel-Technique

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## ABSTRACT

A sol-gel method for the preparation of transparent copper nano particle-containing SiO$_2$ coatings on glass has been developed. The sol is synthesised from alkoxysilanes and tetra ethyl orthosilicate with copper ammine complexes, prepared from Cu$^{2+}$ salts and amino alkoxy silanes. Glass substrates are coated by dipping and layers up to 1μm in thickness are obtained after thermal densification at temperatures between 200 °-500 °C. The Cu colloid formation can be achieved using a reducing atmosphere during densification. Thus reddish-brown coloured coatings on glass with optical densities between 0.5 and 2 are obtained. Under ambient air the colour turns from reddish-brown to dark green. This process is reversible and by re-heating under reducing conditions the reddish-brown colour can be re-established. UV-VIS absorbance measurements and structural investigations by WAXS, TEM, ESCA and SNMS show that the green colour is due to an oxide layer at the colloidal interface.

Key Words: copper, coatings, metal colloids, nano composites, sol-gel-process, electronic structure, ESCA, optical properties

## 1. INTRODUCTION

The use of copper for the production of reddish-brown colours in glasses is known for a long time as copper ruby glass[1] and since this century it is known that nanosized metallic Cu particles - Cu colloids - are responsible for the colouring effect that can be described by the MIE theory[2]. Besides producing metal colloids in glasses by melting or ion-exchange the sol gel process offers a method to obtain them in organic-inorganic and glass-like matrices[3, 4, 5] and to produce coatings. Recently a special synthesis route has been developed for the generation of noble metal colloids (Au, Ag, Pd) in sol gel coatings[6, 7, 8] using functionalised silanes (e. g. aminosilanes, thiosilanes) for the stabilisation of the noble metal ions in the sol, and thus allowing to control the colloidal growth during simultaneous densification of the matrix. For this reason, it was of interest whether this route can be applied for producing copper colloids in a similar way.

## 2. EXPERIMENTAL

For the preparation of coatings containing copper colloids 464 mg Cu(NO$_3$)$_2$ · 2,5 H$_2$O is dissolved in 5 ml ethanol and N-(2-aminoethyl)-3-aminopropyl trimethoxysilane (DIAMO) is added in a molar ratio of 1:1. 15 ml of the SiO$_2$ matrix sol, prepared from 3-glycidoxypropyl triethoxysilan (GPTS) and tetra ethyl ortho-

silicate (TEOS), dissolved in 240 ml ethanol and prehydrolysed with 27 ml of 0,1 m HCl, is added to the alcoholic copper solution. The solution is heated up to reflux and an excess of DIAMO is added to this solution and stirred for 10 minutes. Microscopic slides are dipcoated with withdrawal speeds up to 7,5 mm/s. The resulting coatings are densified at temperatures between 200 °C and 500 °C in a reducing atmosphere (92 % $N_2$, 8 % $H_2$). Under these conditions simultaneous colloid formation takes place. The coloured films were investigated by UV-VIS spectroscopy (Bruins Instruments OMEGA 30), TEM (JEOL JAM 200) and WAXS (Siemens D500 diffractometer). A profilometer (SAS Nanosurf 488) was used to determine the thickness of the coatings on the substrate.

ESCA investigations were carried out using a Perkin-Elmer Spectrometer with non-monochromatised Mg-Radiation (250 W) and a pass energy between 23.5 eV and 117.4 eV. A satellite correction was performed in all spectra. The angle between sample surface and analyser was 45°. Due to the highly insulating properties of the samples, a homogeneous and constant positive charging of the samples was observed during the photoemission process. This causes a shift in binding energy between 4.0 and 4.2 eV compared with the Si 2p-line which was taken as energy reference and set at 103.3 eV. With this reference, the corrected binding energies for the O 1s- and the C 1s-line were 532,7 eV and 284,9 eV respectively for the investigated samples, which is consistent with published data for $SiO_2$ [9, 10] and carbon surface contamination. Before introducing the samples into the UHV they were cleaned with isopropanol. In the UHV, no further treatment of the samples was performed to prevent any change in the electronic structure. Therefore a part of the observed C 1s-signal at 284,9 eV has to be contributed to remaining surface contamination. SNMS (sputtered neutral mass spectroscopy) depth profile analysis of the sample composition was carried out with $Ar^+$-ions with a kinetic energy of 420 eV and a current of 1 mA/cm$^2$. Near the surface region the current was reduced to enhance the resolution and only the elements Cu and Si were detected.

# 3. RESULTS AND DISCUSSION

For the preparation of the SiO$_2$ coatings containing Cu colloids a synthesis route has been developed as shown in fig. 1.



Fig. 1: Flow chart of the preparation for coatings containing Cu colloids via the sol-gel process
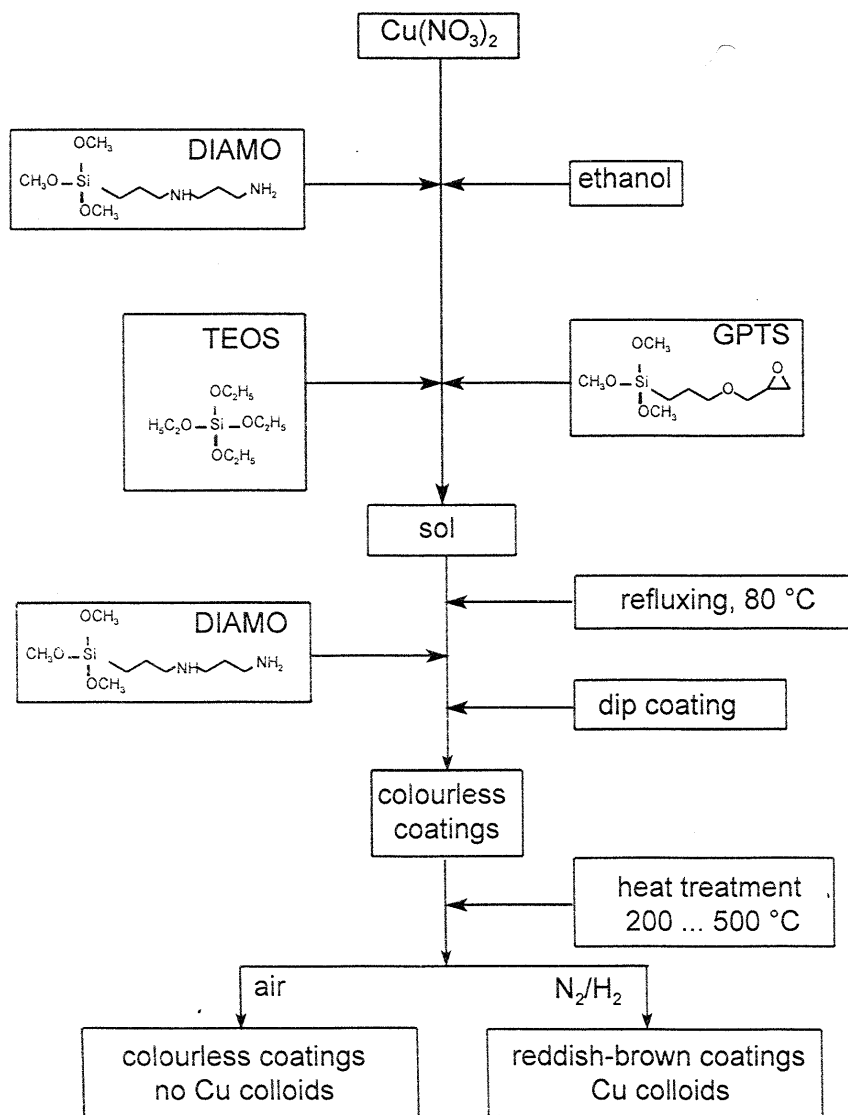
Cu(NO$_3$)$_2$·2,5 H$_2$O was chosen as a precursor for Cu due to its good solubility in ethanol and the low decomposition temperature of transition metal nitrates so that no probably disturbing residues remain in the coatings after firing. Cloudy coatings were obtained after drying at 80 °C and it is assumed that Cu$^{2+}$ containing precipitates are responsible for this effect. In order to prevent the precipitation of copper, DIAMO was added as a complexing agent to form copper ammine complexes. Adding DIAMO to the ethanolic solution of the copper salt, the colour turned from pale blue to dark blue, typically for copper ammine complexes. No precipitation occurs under these conditions and the coatings remain transparent after 80 °C drying and show a slightly blue colour. Heating under ambient atmosphere between 200 °C and 500 °C provided crackfree and transparent but nearly colourless coatings with thicknesses between 0.4 and 1.2 µm. Since the reddish-brown colour (attributed to a Cu colloid formation) is only obtained in a reducing atmosphere, it is concluded that the reduction of Cu$^{2+}$ ions by organic decomposition

products, formed during the thermal densification treatment of the coatings, is suppressed in the presence of oxygen. UV-VIS spectroscopy of the tempered samples exhibits the typical plasmon band for copper colloids. Fig. 2 shows an absorbance spectrum of a sample with 0.4 µm film thickness and a total Cu content of about 0.1 mol/l and the calculated spectrum using a calculation programme[11], based on the MIE

theory[2] assuming a refractive index of $n_D = 1.52$, a colloid radius of 10 nm and a volume concentration of colloids of $c = 1.2 \cdot 10^{-5}$.
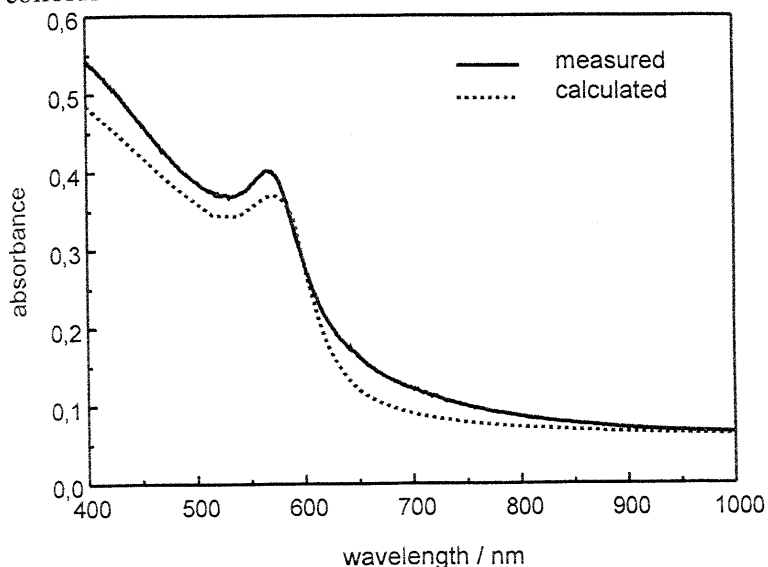


Fig. 2: Measured absorbance spectrum of copper colloids in a silica coating densified at 500 °C while reducing atmosphere (92% $N_2$, 8% $H_2$) and a calculated spectrum based on MIE's theory ($n_D = 1.52$, R = 10 nm, c = 1.2 $\cdot$ $10^{-5}$)
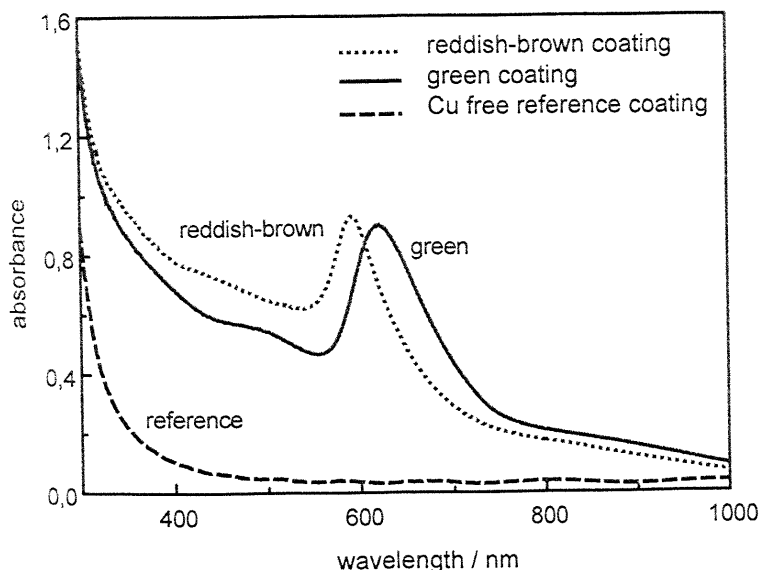


Fig. 3: Measured absorbance spectra of a reddish-brown and a green coating derived from the same sample first tempered in a reducing atmosphere (92 % $N_2$, 8 % $H_2$) and then stored for 24 h in air and a reference coating without copper

As one can see from fig. 2 reasonable agreement between the measured and the calculated curve is obtained. The measured plasmon band of the sample is slightly broader than the calculated spectrum. This is possibly due to a broader size distribution of the colloids. By storing the samples heated at 200 °C in an ambient atmophere the colour turns slowly from reddish-brown to green. By temering the green samples in a reducing atmophere the reddish-brown colour can be re-established. Storing the samples in a nitro-en atmosphere does not alter the reddish-brown colour With 500 °C treated samples no coour change takes place even after several days in the reduced samples.

In the UV-VIS spectrum the change in colour from reddish-brown to green is accompanied by a shift in the plasmon band to longer waveengths as shown in fig. 3 for one and the same samle. It is obvious that the colour of the green sample is also due to an absorbance band very similar to the plasmon band of coper colloids. The new absorbance band is shifed to longer wavelengths and broadened compaed to the original plasmon band. From the influence of the redox potential of the atmosphere on the coatings, it is assumed that the reversible colour change from reddish-brown to green can be attributed to a redox process. The similarity of the two absorbance bands (fig. 3), including the interband absorbance region, indicates that Cu colloids are still present in the green coating. The shift of the peak position to longer wavelengths may be attrib-uted to a surface layer at the colloids with an increased refractive index as one might conclude from spectra calculated for a fixed colloid radius and colloid concentration but different refractive indices between 1.5 and 2.2. The broadening of the

band indicates a decreased size of the metallic Cu particles. Thus it is assumed that the green colour is due to Cu colloids with an oxidised surface layer, e. g. a Cu core with smaller size and a dielectric interface with increased refractive index. In order to check this hypothesis the microstructure of the reddish-brown and green coatings was investigated.
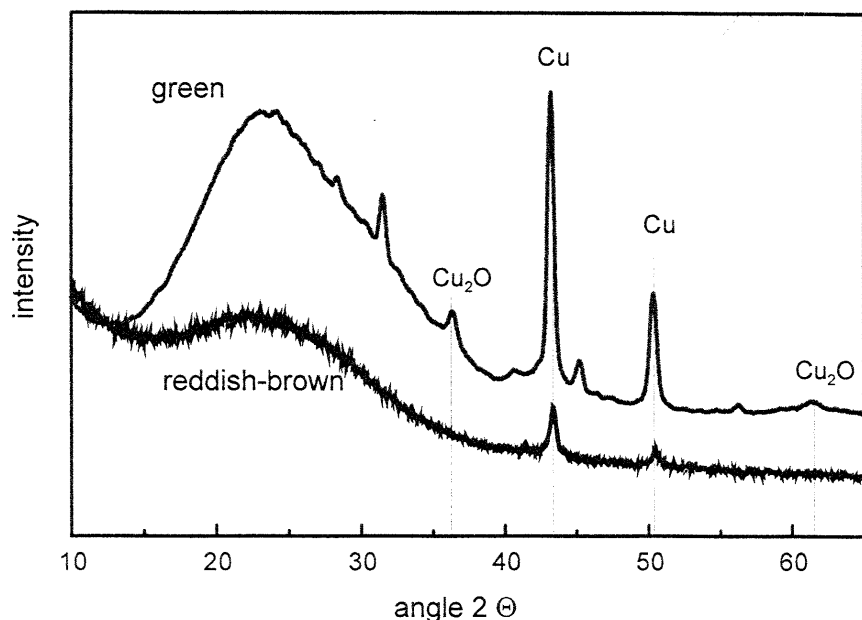


Fig. 4: WAXS spectra of a reddish-brown coating (film on substrate) and green coatings (scratched powder)

Fig. 4 represents WAXS measurements of a reddish-brown coating (thin film set-up) and a powder of a green coating scratched from the glass substrates. Both samples exhibit peaks belonging to metallic copper. In the green sample additional reflexes are obtained. Some of them correspond to copper oxides. Although a doubtless identification of copper oxide is not possible by WAXS, the measurements clearly proof the existence of Cu particles in the green coatings.

A green and a reddish-brown sample was examined by TEM with an acceleration voltage of 200 keV and selected area diffraction patterns were made. The green sample contains particles in the range of 5 nm - 30 nm in diameter with a mean diameter of about 15 nm, possessing to a crystalline structure which results from the diffraction contrast of the pictures which in turn is caused by the contrast of thickness in some of the particles. In fig. 5, the TEM picture of the green coating is presented. No visual difference was observed in the particles of the reddish-brown and the green sample. Selected area diffraction pattern of a reddish-brown coating reveals, in addition to broad diffraction rings caused by amorphous structures (carbon film and sol-gel matrix), some weak but sharp diffraction rings caused by crystalline particles with Laue reflexes (spotlike reflexes of diffraction). The evaluation of these reflexes and the comparison to ASTM values showed agreement as far as the reflexes of metallic copper are concerned. In fig. 6 the picture of a selected area diffraction pattern of a green coating is presented. In this picture, the same reflexes as of a reddish-brown coating are recognisable as belonging to metallic copper but additionally, there are two more, respectively weak but sharp diffraction rings not containing Laue reflexes and not belonging to copper. These weak reflexes (marked with arrows in fig. 6) indicate a second crystalline phase. The evaluation of these reflexes is a further indication for a copper oxide phase. The TEM pictures, however, gave no hint of a second type of particles. This is in agreement with the UV-VIS absorbance spectra that show no further absorbance band but only a shift in the plasmon band of the copper colloids.
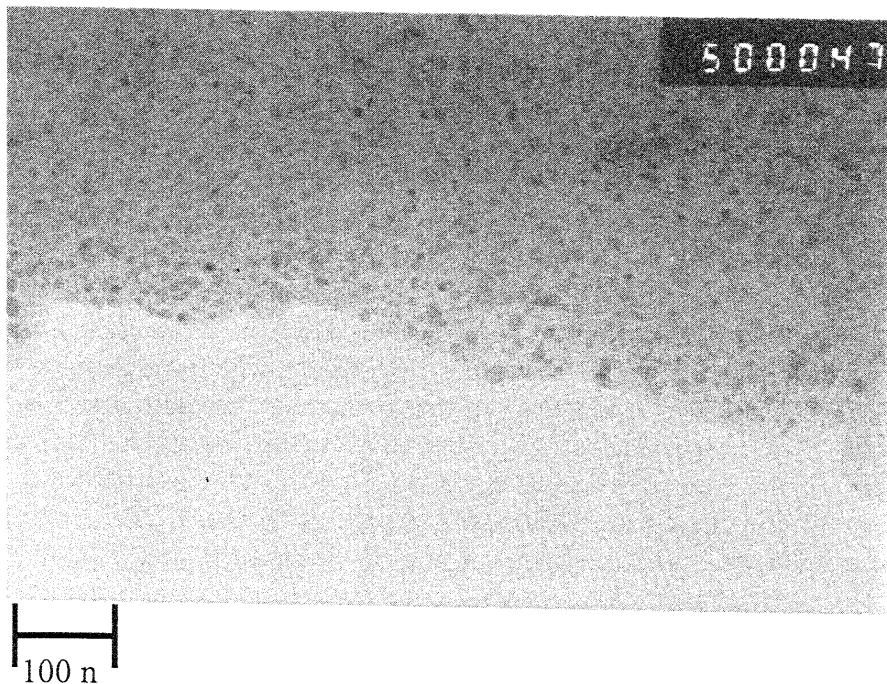
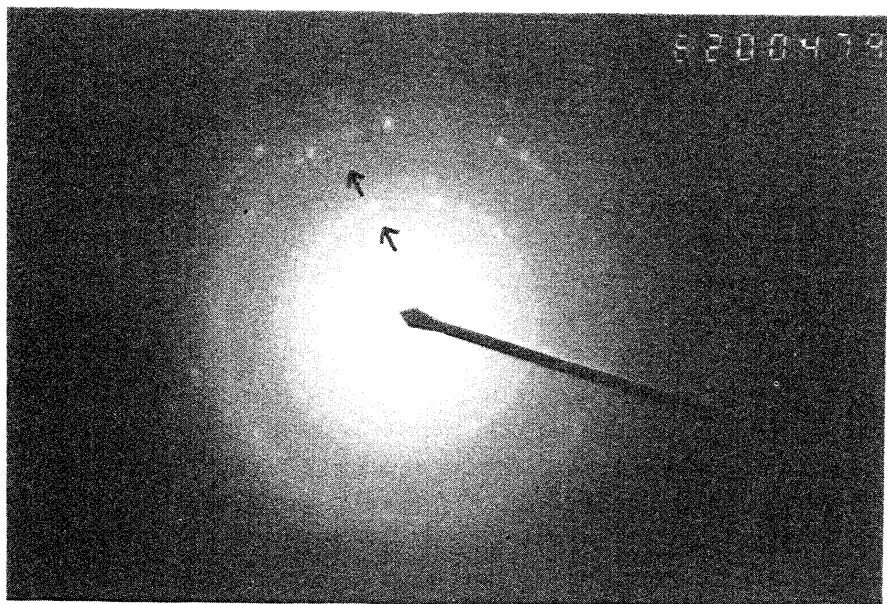Fig. 5: TEM picture of copper colloids in a green coating



Fig. 6: Picture of a selected area diffraction pattern of a green sample (acceleration voltage 200 keV, camera length 82 cm, magnification of the picture n = 2,3), containing diffraction rings and Laue reflexes of metallic copper and two additional diffraction rings marked with arrows.

These results strengthen the hypothesis of a copper oxide layer around the copper colloids. To obtain detailed information about the electronic structure of the copper, ESCA and SNMS investigations were carried out on a green and a reddish-brown sample reduced at 200°C and 500°C respectively. The green samples changed their originally reddish-brown colour in ambient air.

A detailed analysis of the Cu $2p_{3/2}$-line at both samples is shown in fig. 7 and fig. 8 respectively. The Cu $2p_{3/2}$-spectrum of the reddish-brown coating (fig. 7) shows at the beginning of the ESCA measurements clearly two components at 932.7 eV and 930.5 eV binding energy (ref. to Si 2p). The fraction of the low energy component is at first about 25-30% of the main line. The very weak shake-up satellite at about 942 eV which is typical for copper with an unfilled 3d configuration disappears after some minutes of X-ray irradiation completely, indicating an electronic structure of the copper in the sample close to $3d^{10}$. The main line at 932.7 eV is associated with metallic copper colloids in the coating in very good accordance with[10] and the electron diffraction and WAXS results. This confirms the energy reference chosen and the reliability of the analysis. The shoulder of the main line at about 930,5 eV has an even lower binding energy as in the case of metallic copper, indicating that the copper in this compound formally has a slightly negative valence. Any copper oxide can be excluded. The observed shoulder could be attributed to copper compounds like a copper-cyano or a copper-carbonyl compound[10]. Although this component is not observed after densification at 200 °C (fig. 8), an attribution to residuals of the Cu-DIAMO complex cannot be excluded. Carbon radicals formed by crack processes at higher temperatures might react with copper. An other explanation might be a surface effect like a reaction of a part of the copper colloids at the surface of the coating with carbon or nitrogen from the reducing atmosphere which did not take place at the lower temperature (200°C) in the case of the green sample. As a function of X-ray irradiation time, the shoulder at 930.5 eV is decreasing very fast and after 40 min only metallic copper can be found in the sample. This could be a hint for a rather weak binding and an electron sensitive compound and might be a further confirmation for the interpretation of the shoulder as a kind of copper surface compound. The green coating has a rather different Cu $2p_{3/2}$-spectrum (fig. 8) compared with the reddish-brown one in fig. 7. At the beginning, the Cu $2p_{3/2}$-line consists of two components at 934.5 and 932.2 eV (ref. to Si 2p) with an intensity ratio of about 7:3. One can also see a rather strong shake-up satellite. As a function of X-ray irradiation time the intensity ratio between the two components is changing continuously. After 4 minutes both signals show nearly equal intensity (lower spectrum in fig. 8) and after 90 min, the high energy component can be resolved only as a weak shoulder of the main peak. At the same time the binding energy of the main peak shifts towards 932.7 eV. The loss of intensity in the high energy component is correlated to the decrease of the intensity of the shake-up satellite.

The component at 932,7 eV has to be attributed to metallic copper. The small shift of about 0.5 eV in binding energy may be due to the low statistics in the lower spectrum. The high energy component with a binding energy of about 934,5 eV is more difficult to interpret. The analysis of the ESCA spectra of the other elements in the coating (Si 2p, N 1s, C 1s and O 1s) led to the conclusion that oxygen was the most probable binding partner of Cu, but $Cu_2O$ has a much lower binding energy and can be excluded and pure CuO has an energy in the range of 933.9 eV which is still too low to explain the observed binding energy. On the other hand, the strong satellite intensity indicates a charge transfer to the copper during the photoemission process and a Cu configuration near $3d^9$. Therefore this component has to be attributed most likely to a copper oxide in the form of a mixture of formal two and three valent copper as in a spinell-like structure like $Cu_3O_4$ for example. This interpretation is in accordance with the electron diffraction and WAXS results, where in both cases the best fits were obtained for copper oxides, but the oxide could not be identified as any pure copper oxide like CuO and $Cu_2O$.

The copper oxide compound in the green coating (fig. 8) is rather sensitive to X-ray irradiation and rapidly reduced to metallic copper, which signal was rather low at the beginning of the measurements.
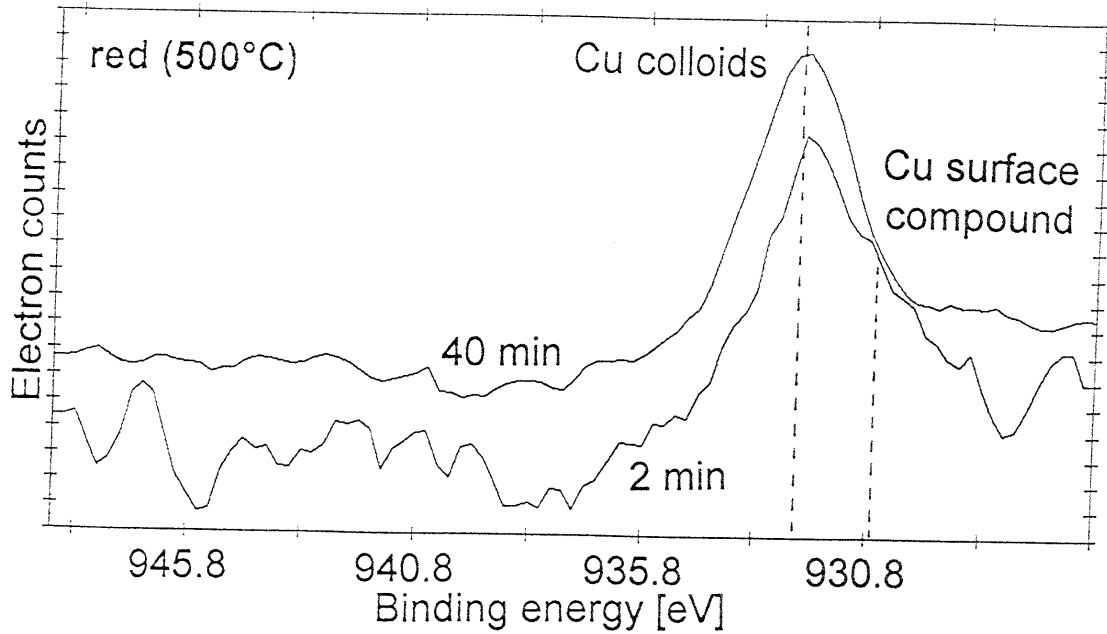


Fig. 7: ESCA spectra of the Cu $2p_{3/2}$ line for the reddish-brown sample (500°C). The lower spectrum is taken within the first 2 min, the upper spectrum after 40 min of the ESCA mearsurements at the same position
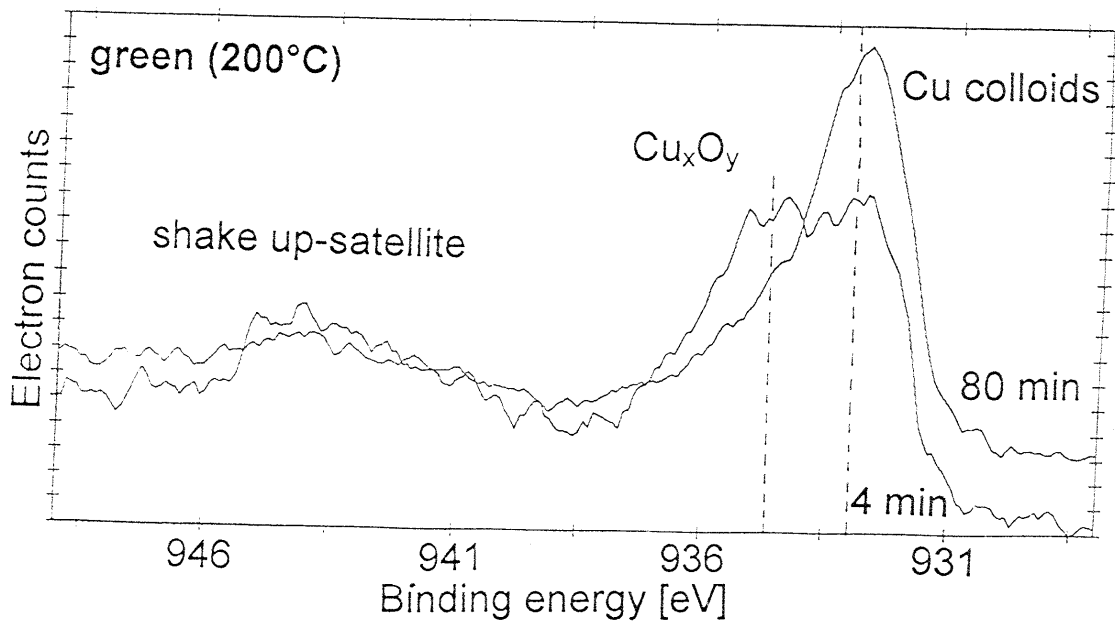


Fig. 8: ESCA spectra of the Cu $2p_{3/2}$-line for the green sample (200°C). The lower spectrum is taken within the first 4 minutes, the upper spectrum is taken after 80 min of the ESCA measurements at the same position

In this context it has to be taken into account, that the metallic copper which was found by WAXS and TEM investigations in the green coatings could be partially an artefact because of strong and rather long electron and X-ray irradiation.

To explain the observed Cu $2p_{3/2}$ spectrum in fig. 8, a model of a nucleus of metallic copper in the colloids coated by a layer of a copper oxide similar to $Cu_3O_4$ is proposed. In this model, a rough estimation of the average thickness of the oxidic cover from the ESCA data leads to a mean thickness of the layer at the beginning of the X-ray irradiation of about 0.6 - 0.8 nm. This is reduced to about 0.1-0.2 nm in average at the end of the measurements. If metallic colloids with and without an oxide coverage would exist simultaneously in the coating, the thickness of the oxide film would be higher than calculated here, but the TEM and UV-VIS experiments gave no evidence for such an assumption. The observed reduction of the copper oxide during X-ray-irradiation fits very well to the proposed model because highly dispersed copper is well known in photo-electron-spectroscopy to act as reducing agent in contact with copper oxide which is normally stable under X-ray-irradiation[12, 13].

The SNMS investigations showed no great differences between reddish-brown and green samples. The very similar depth profile of the elements in both type of samples gives no evidence for a change in colour as a function of the annealing temperature due to different elemental distributions in the samples. Therefore the colour of the coatings is affected solely by the electronic structure of the copper colloids.

## 4. CONCLUSION

The investigations have shown that reddish-brown $SiO_2$ coatings containing copper colloids can be prepared via an organic-inorganic sol-gel-processing route, using an aminosilane for the stabilisation of Cu- ions in the sol-gel transition. The change of colour into green is interpreted as a surface oxidation of the metallic copper colloids due to oxygen migrating into the coatings, leading to remarkable and reversible changes in the optical properties.

For the future work a theoretical description of the optical properties of metal colloids with a dielectric shell, embedded in a dielectric matrix with different refractive indices has to be developed, that could be based on already known models for metal particles with metallic shells in a dielectric matrix[14, 15, 16] and the structural investigations should be completed including HTEM and ASAXS measurements.

Additionally the influence of the oxide shell around the Cu colloids on their non-linear optical response will be studied, since an enhancement of the local field factor caused by an interfacial region with increased refractive index may be assumed, that could lead to nano composite coatings with high third order susceptibilities.

## 5. ACKNOWLEDGEMENT

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