C.L.O.E.S
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PROCEEDINGS

FOURTH SAAR-LOR-LUX MEETING on Functional Advanced Materials

at

TECHNOPÔLE DE METZ
CLOES
UNIVERSITE DE METZ-SUPELEC

FRANCE

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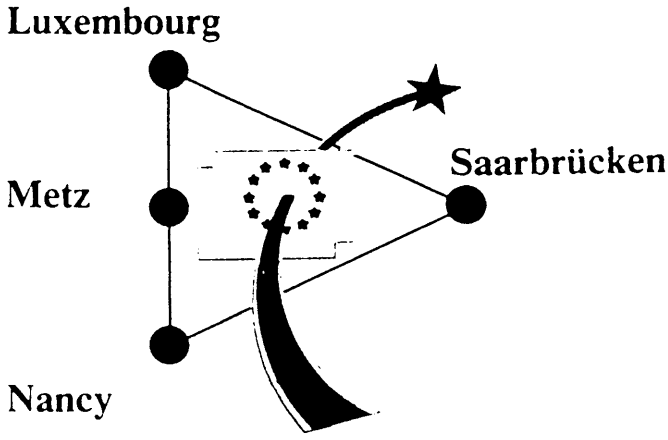

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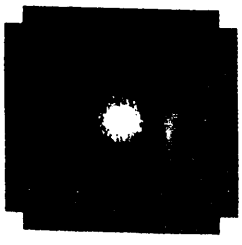

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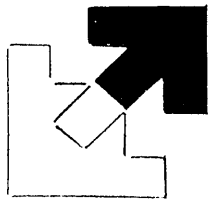

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The meeting is held on the Campus of Supelec-Metz and is included in the events of its Centenary.

Sol-Gel-Synthesis of Ag-colloid containing Lead-Silica-Coatings and Investigation of their optical Properties

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Abstract

1. Introduction

Metal colloids can be used to produce coloured coatings on glass due to their high molar extinction coefficients. With non-spherical colloids interesting optical effects can be achieved because colour and polarization of the transmitted light can be tuned in a wide range via the eccentricity of the particles. One way to prepare spheroidal colloids is to establish spherical colloids in glass by melting or ion-exchange and following thermal treatment. Afterwards this glass is reheated above T_g and deformed by an uniaxial tension as shown in the case of Ag- and Au-colloids[1,2]. In order to investigate whether this method can be applied to colloids in sol-gel derived glasslike coatings on glass it is necessary to develop coatings with thermo-mechanical properties adapted to the glass substrate. For a first approach a synthesis route to Ag-colloids in a lead-silica-coating was developed, leading to a glass with 45 wt% of PbO and a T_g of about 480°C.

2. Experimental

$AgNO_3$ and $Pb(CH_3COO)_2$ were dissolved in methanol and afterwards complexes with $NH_2(CH_2)_2NH(CH_2)_3Si(OR)_3$ (DIAMO) in a molar ratio of 1:1 were formed. A transparent solution is obtained, which also can be mixed with a prehydrolised SiO_2-sol containing γ-glycidoxy propyl trimethoxy silane and tetra ethoxy silane without any Ag or Pb compound precipitated. This method allows to achieve crackfree coatings after thermal treatment at 150°C - 700°C with a thickness from 0,5 to 1,2 µm on fused silica slides.

3. Results

Fig. 1 shows the result of the UV-VISspectroscopy. In the Ag free but Pb and DIAMO containing reference coating (7R) a band at a wavelength of about 250 nm (7R) can be observed which is typical for Pb-ions. From ESCA analysis it can be concluded that the electronic structure of the Pb is pure ionic in the whole range of densification temperatures. A refractive index of about 1.6 was measured after densification at 500°C, which also indicates ionic lead in a silica network.

The Ag containing lead-silica-coatings densified at 150°C show a distinct absorption peak at about 350 nm which can be attributed to atomic silver. A weak shoulder at about 440 nm might be an effect of small Ag-colloids already formed. The slightly yellow coatings densified at 200°C and 300°C clearly show a plasmon band typical for Ag-colloids. The peak position is at relatively long wavelengths (440 nm) which may be attributed to the increased refractive index caused by silver- and lead-ions and to the very small size of the colloids of about 4 nm, as determined by WAXS and TEM. The intensive absorption band of the yellow coloured coating densified at 400°C is shifted to shorter wavelengths. This trend is continued in the case of the yellow brown coloured coating densified at 500°C and 600°C. At 700°C the coatings show a sharp absorption peak attributed to the typical absorption band of silver colloids.

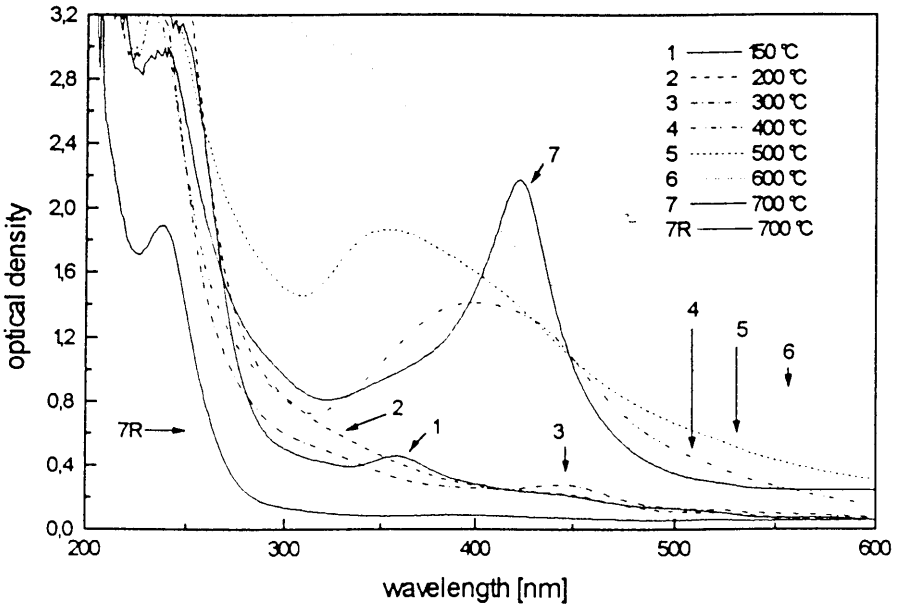

Fig. 1: Absorption spectra of Ag free (7R) and Ag containing PbO-SiO_2-coatings on fused silica for different temperatures of densification, reference air

From WAXS and TEM investigations it is concluded that Ag crystallites are growing in the range between 300°C and 700°C from 4 nm to 28 nm. This should lead to a remarkable narrowing and a very slight shift of about only a few nm to shorter wavelengths, as it is concluded from theoretical investigations[3].

But the absorbance spectra for 400°C, 500°C and 600°C are absolutely untypical for Ag colloids. For their explanation influences from partially burnt organic residuals have to be taken into account as well as interactions between Ag and Pb compounds (Pb, PbO, PbO_2). It has also be taken into consideration that phase seperation processes could take place and seperated inhomogeneities could also be dissolved by thermal treatment at about 700°C that is much higher than the T_g of the coating material. For the investigation of these interesting questions microstructural investigations by HTEM and XPS will be carried out in the future.

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[3] B. Dusemund, Diplomarbeit, Saarbrücken 1991