

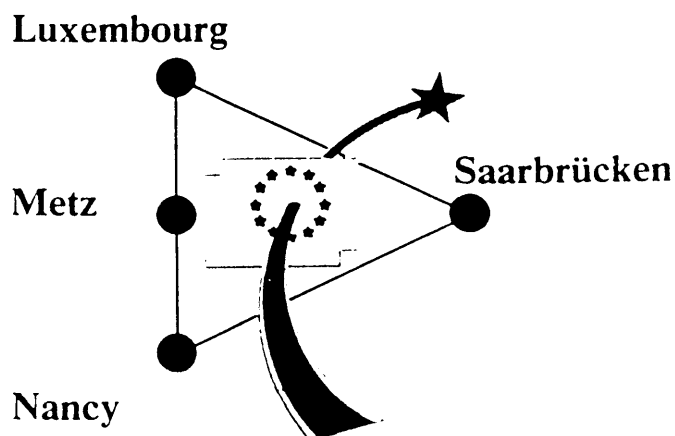
PROCEEDINGS

**FOURTH SAAR-LOR-LUX MEETING
on Functional Advanced Materials**

at
**TECHNOPÔLE DE METZ
CLOES
UNIVERSITE DE METZ-SUPELEC**

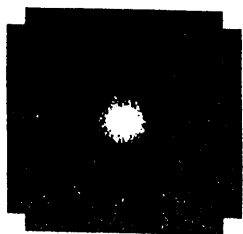
FRANCE

NOVEMBER 24-25 1994

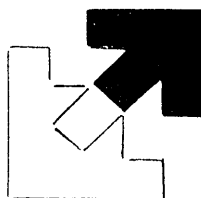


INTENSIVE COURSES

supported by
the European Community COMETT
via Euro Materiaux



**Pôle Universitaire
Européen Nancy-Metz**



Université de Metz



Campus de Metz

XPS-Investigations to the Influence of the Interface Colloid-Matrix on the Electronic Structure of Noble Metal Colloids in Organic/ Inorganic Sol-Gel-Coatings on a Glass Substrate

B. Kutsch, M. Schmitt, M. Mennig and H. Schmidt

Institut für Neue Materialien gem. GmbH, Im Stadtwald, 66123 Saarbrücken, Germany

Abstract

1. Introduction

The preparation of noble metal colloids in glass-like sol-gel-coatings on glass substrates is of interest because of their optical properties (high molar extinction coefficients, high temperature stability, non-linear optical properties, decorative applications). In recent publications [1-4], the successful preparation and optical characterisation of such coatings has been reported in case of Ag, Pd, Au and Cu. The colloid formation process is controlled by bifunctional ligands and thus the interface colloid to matrix that also has an influence on the optical properties of the system, plays a very important role. A systematic investigation of the electronic structure of these colloids with special stress on the interface colloid to the surrounding matrix has not been performed yet. Temperature and atmosphere during densification of the coatings, composition of the matrix, composition of the substrate and shape of the colloids are possible parameters which could change this interface.

2. Results

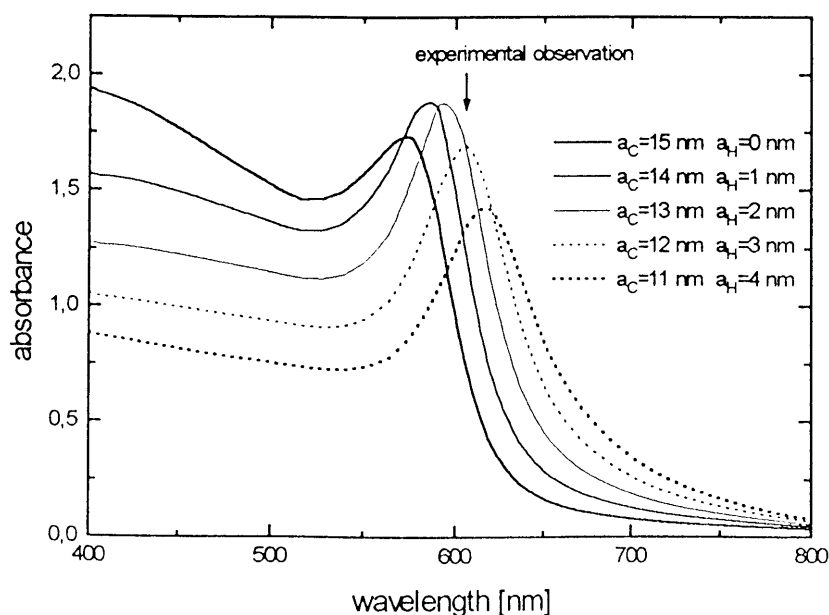


Fig. 1: calculated UV-VIS spectra [5] using the Mie-theory within the model of a metallic Cu nucleus coated with a shell of CuO with various thickness in a dielectric matrix ($n_D=1,52$). a_C : size of the metallic nucleus, a_H : size of the oxidic shell, mean size of the colloids: 15 nm, arrow: experimental result [4].

To give an example to one aspect of the enormous influence of the interface to the physical properties of the coatings, fig. 1 shows a theoretically calculated optical spectrum for a Cu colloids containing coating using the Mie-theory. In this model it is assumed, that a nucleus of metallic Cu colloids (mean size: ~15 nm) is coated with a CuO shell with different thicknesses. The spectra resulting from this calculation as a function of the thickness of the shell fit very good to the experimental UV-VIS and XPS data published in [4] and prove the model proposed there if a mean thickness of the oxidic shell of about 2 - 3 nm is assumed. The aim of this paper is to demonstrate that the combination of UV-VIS spectroscopy and XPS offers a wide and detailed set of information about the electronic structure of the colloids. Beneath a quantitative analysis of the composition of the coatings and the structure of the valence band, XPS offers a direct account to the core binding energies and thus to a determination of the valences of the investigated elements. Fig. 2 shows a XPS 4f-core spectrum of Au colloids in a sol-gel-matrix, prepared as described in [3] on a soda lime glass.

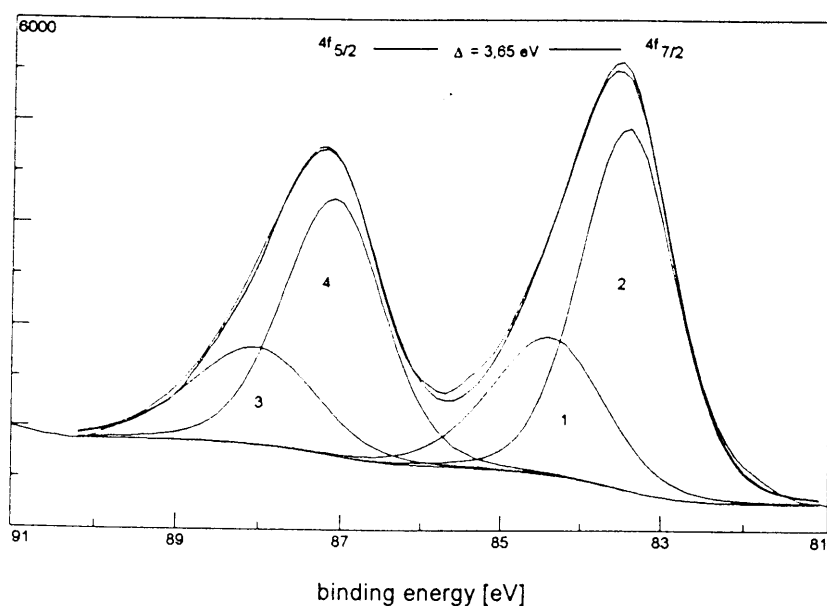


Fig. 2: XPS spectrum of the Au 4f lines of Au colloids in a sol-gel-matrix densified at 300°C on a soda-lime glass substrate. The binding energies indicated were referred to C 1s=284.6 eV

Two components with a binding energy of 84,45 eV (1) and 83,48 eV (2) can be resolved. The first component is attributed to metallic Au whereas the second component could be ascribed to a formally negative valence of Au. As this component is not observed when fused silica is used as a substrate instead of soda lime glass it is hypothesised that this component is due to an interaction of the surface of the Au colloids with Na^+ ions, which diffuse into the sol-gel-matrix from the substrate as determined by SNMS. In detail, it could be attributed to the formation of an Au-compound at the surface of the colloids or to a charge transfer from the nucleus to the surface. Both assumptions would imply a different dielectric function at the surface of the colloids compared with the nucleus. The observed binding energy component (2) is much lower than in the case of metallic Au (84 eV) and can not be explained only as a pure physical effect similar to ref. [6-8] in the case of small Au-colloids which showed a binding energy shift of about 0.25 eV to higher values due to final state

effects. In the contrary, such final state and size effects for small colloids probably contribute to the energy difference of 0.45 eV of the "metallic" component (1) in fig. 2 to the bulk value for metallic gold at 84 eV. Bulk Au-compounds with such low Au 4f-core energies as in component (2) are not known in the literature. Any effect due to improper energy reference can be excluded since the binding energies for the Si 2p lines and the O 1s-line were 102.88 eV and 532.32 eV respectively which are typical values for soda-lime glasses [9]. At present HTEM and UV-VIS investigations are carried out to study these coatings in detail to get more information about the surface and shape of the Au colloids and to clarify whether this effect also can be explained by a nucleus-shell-model. Au colloids with surface layers of different electronic structure are very interesting for non-linear optical investigations as the dielectric function at the surface has a strong influence on the $\chi^{(3)}$ -effect. Further work will be concentrated in this field and in the systematic preparation of such effects.

The authors thank the Deutsche Forschungsgemeinschaft and the State of Saarland for financial support and J. Rostalski who performed the calculation of the spectra in fig. 1.

3. References

- [1] A. Hinsch, A. Zastrow, J. Non-Cryst. Sol. **147&148** (1992), 579-581
- [2] T. Burkhart, M. Mennig, H. Schmidt, A. Licciulli, Proc. MRS Spring Meeting San Francisco 1994
- [3] M. Mennig, M. Schmitt, U. Becker, G. Jung, H. Schmidt, SPIE Meeting Sol-Gel- Optics III, San Diego 1994, to be published
- [4] M. Mennig, M. Schmitt, B. Kutsch, H. Schmidt, SPIE Meeting Sol-Gel-Optics III, Dan Diego 1994, to be published
- [5] J. Rostalski, RWTH Aachen, private communication
- [6] M. Quinten, I. Sander, P. Steiner, U. Kreibig, K. Fauth, G. Schmid, Z. f. Phys. D, **20**, (1991), 377-379
- [7] S. B. Diczynski, G. K. Wertheim, Comm. Sol. State Phys. **11** (1985), 5, 203-219
- [8] P. H. Citrin, G. K. Wertheim, Phys. Rev. B, **27** (1983), 6, 3176-3200
- [9] Th. Gross, Ramm, Sonntag, Unger, Weijers, Adem, Surf. & Interf. Anal. **18** (1992), 59-64