

# Surface and interface effects in the optical properties of silver nanoparticles

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**Abstract.** We present novel experimental results about influences of surrounding foreign materials on optical properties of small silver clusters. First we show spectra of *free* cluster beams produced with different seeding gases Ar, Kr, Xe. Second, we estimate, from measured spectra, the cluster deformations and contact areas after *deposition* on different substrates ( $\text{Cr}_2\text{O}_3$  and  $\text{MgF}_2$ ) at room temperature and on  $\text{SiO}_2$  at 110 K and between 160 K and 300 K. Third, we present and compare the *static and dynamic charge transfer* after *embedding* the clusters in various fluorides and compare with previous results on oxides.

**PACS.** 73.61.-r Electrical properties of specific thin films and layer structures (multilayers, superlattices, quantum wells, wires, and dots) – 77.55.+f Dielectric thin films – 78.20.Ci Optical constants (including refractive index, complex dielectric constant, absorption, reflection and transmission coefficients, emissivity)

## 1 Introduction

The optical properties of Ag clusters in the visible are governed by the Mie plasmon resonance, which proves to be, to an extraordinary amount compared to all other metals, sensitive to properties of the cluster surface, to influences due to changes of structure, shape, size, etc. and to the presence of surrounding foreign material (adsorbates, substrates, embedding host media) [1, 2]. In particular, we observed that *static and dynamic charge transfer* can occur through the interface, when the clusters come into direct contact to foreign materials [3].

As a consequence, if clusters, or, more general, nanostructured components in composite media are in contact with surrounding foreign material, electronic interface effects occur which often influence their properties more severely than the well-known size effects. Such structural elements can thus not be treated as self-contained, independent units.

## 2 Experimental arrangement and measurements

Silver clusters were produced by a thermal evaporation, gas expansion source which was described in [3]. Optical absorption measurements in  $1.5 \leq \hbar\omega \leq 5$  eV were performed in-situ in a connected UHV experiment chamber (a) at the free beam and (b) after deposition of the same clusters on chemically cleaned substrates, with or without simultaneous additional evaporation of embedding materials. Polarization and angle of incidence of the incident

light could be varied in order to analyse the cluster shapes in detail after deposition on different substrates. In addition, we changed the temperature of the substrate for deposition down to 110 K or 160 K. In the latter experiment, we varied the temperature after deposition between 160 and 300 K to obtain further information about the cluster deformation. TEM characterization of clusters produced with Ar gas on graphite yielded  $2.0 \pm 0.5$  nm in diameter.

## 3 Experimental results and interpretations

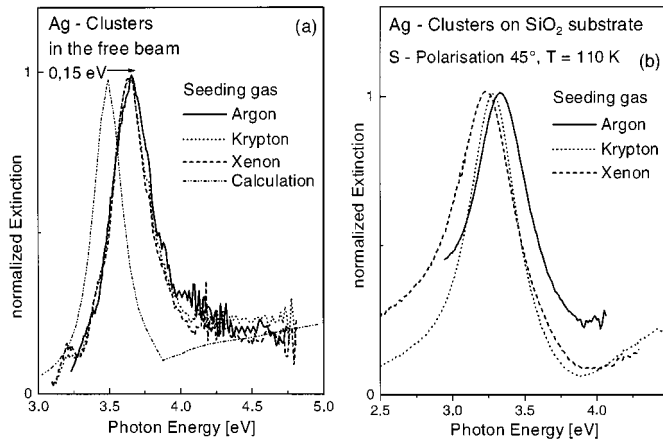
### 3.1 Absorption measurements on the free cluster beam

Figure 1a gives optical absorption spectra from free beams of Ag clusters produced with different seeding gases but otherwise unchanged source conditions. The spectrum with seeding gas Ar was taken from [3]. The spectra are averages of typically >100 single spectra, and error bars in the centre part of the Mie peak are slightly larger than the line thickness. They increase towards the edges of the spectra. The volume-filling factor of  $V_{\text{cluster}}$  to  $V_{\text{beam}}$  was  $\approx 1.5 \times 10^{-10}$ .

Common to all three spectra is the surprisingly narrow plasmon band width. In all three cases, the interband absorption as known from larger clusters, is not yet fully developed.

From the optical spectra which are sensitive to the cluster size, we conclude diameters of the clusters produced in different seeding gases to differ only slightly (less than 30%), if at all. According to the scaling law of Hagenau [4] the diameter would be expected to increase from Ar to Xe. Further TEM and AFM studies are in

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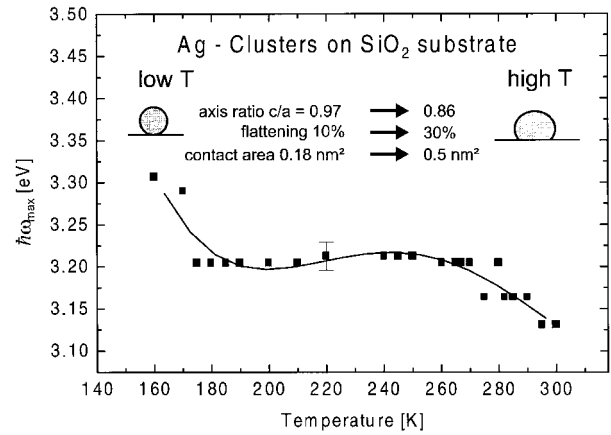
**Fig. 1.** (a) Normalized extinction spectra of free Ag-clusters in the cluster beam produced with different seeding gases: Ar [3], Kr, Xe. (b) Spectra of these clusters deposited on a cold SiO<sub>2</sub> substrate ( $T = 110$  K).

progress to determine sizes also for seeding gases other than Ar and on substrates other than graphite.

### 3.2 Absorption measurements of Ag clusters deposited on different substrates

The clusters, accelerated during the expansion into the UHV chamber [3], hit the substrate surface with a mean velocity of  $\approx 1 \times 10^3$  m/s. Hence, elastic and plastic deformations upon collision from the (initially) spherical shape are expected. The resulting cluster shape also depends on the amount of wetting between cluster and substrate, *i.e.* the relative amount of cluster surface in the *contact area*. Coverages about 0.075 ML were achieved by using a chopper with a slit for 0.002 ML per turn. The coverages were determined, both from the effective quartz balance thickness and, indirectly, from the absorption oscillator strength [1]. At these low coverages previous experiments and TEM and AFM investigations show that there is no coalescence even at room temperature (see *e.g.* Figs. 3 and 5 in [5]), which would strongly influence the optical spectra [6]. Absorption measurements under 45° with *s*- and *p*-polarized light were performed and allowed the quantitative evaluation of the deviations from spherical shape by applying the theory of Gans under the simplifying assumption of flattened spheroidal shape [1].

Evaluating the theory of Yamaguchi [7], which takes into account more realistic cluster shapes and also the electromagnetic coupling between clusters, we were able to derive the size of the average direct *contact area* between Ag clusters and the plane substrate:  $\approx 0.5$  nm<sup>2</sup> in the case of SiO<sub>2</sub> substrate (30% of the cluster surface), and less 0.1 nm<sup>2</sup> in the case of Cr<sub>2</sub>O<sub>3</sub>. Theoretical expectations for the former case are 0.27 nm<sup>2</sup> [8] (all room temperature). Plastic remanent deformation upon wetting is small for deposition on MgF<sub>2</sub> substrate (axis ratio 0.94 at room temperature, Ar seeding gas) and extremely small in the case of Cr<sub>2</sub>O<sub>3</sub>: within the limits of accuracy, the clus-



**Fig. 2.** The maximum of the extinction spectra ( $h\omega_{\max}$ ) of Ag-clusters ( $2R = 2$  nm) deposited at 160 K on SiO<sub>2</sub>, *versus* sample temperature during subsequent annealing to 300 K. Angle of incidence: 45°, *s*-polarisation.

ters are spherical ( $c/a = 0.97$ ), despite the high, for all substrates constant collision velocity. The spheroidal deformation evaluated previously from experiments on SiO<sub>2</sub> glass substrate at 300 K [5] proved to be only small: the average axis ratio  $c/a$  is 0.86.

Figure 1b shows absorption spectra of Ag clusters produced with different seeding gases and deposited on SiO<sub>2</sub> glass at 110 K. These results point to an even smaller deformation upon wetting at lower temperature, yet there are slight differences in peak position for clusters produced with different seeding gases. The electromagnetic coupling [7] between clusters at this coverage causes a blue-shift of +0.08 eV compared to single clusters. Red-shift could be explained by decreasing coupling through increasing size (see Sect. 3.1) but not by differences in mass added at same cluster size. The coverages of  $\approx 0.075$  ML were too small for coalescence [5], which would cause a red-shift.

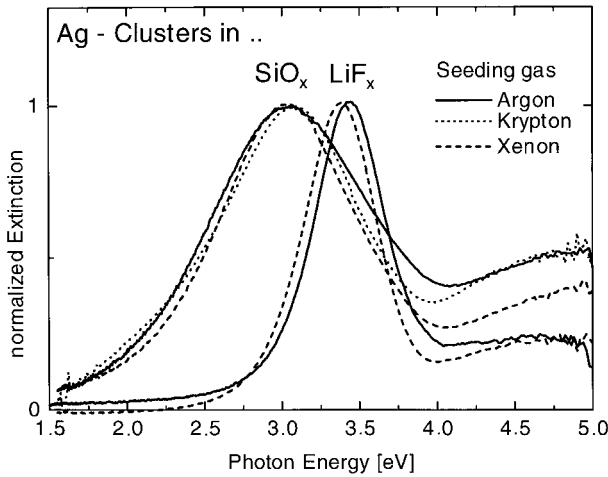
Our experiments with a cooled SiO<sub>2</sub> substrate showed that the ellipticity (Gans theory) and, respectively, the contact area (Yamaguchi) depend on the substrate temperature. In one experiment, clusters were deposited at 160 K and the temperature was then raised slowly. Figure 2 shows the changes of the Mie peak which indicate that  $a/c$ , amounting to 0.97 at 160 K, decreases to 0.86 at 300 K. The according contact areas are 0.2 and 0.5 nm<sup>2</sup> with relative uncertainty of less than 20%.

Compared to former investigations [3,5] the peak position at 300 K differs probably due to a thin layer of H<sub>2</sub>O which evaporates from the cryoshield at sample temperatures of  $\geq 280$  K.

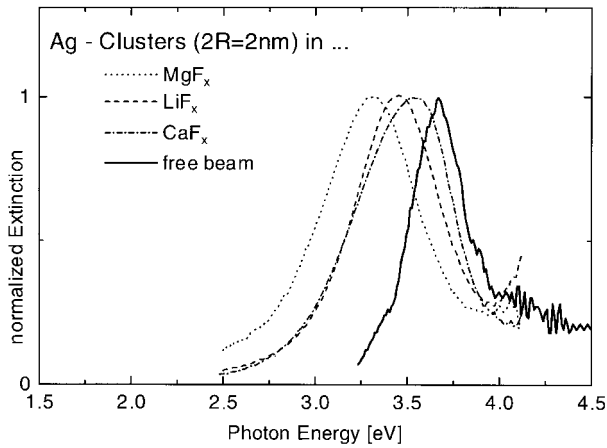
### 3.3 Absorption measurements of Ag clusters embedded in different solid, non-absorbing host media

Embedding the differently seeded clusters in SiO<sub>x</sub> (Fig. 3), there is hardly any difference in peak positions, in contrast to the red shift in LiF<sub>x</sub> (which is consistent with Fig. 1b).

In Figure 4 we present novel results concerning the class of *fluoride* materials. For comparison, the spectrum



**Fig. 3.** Normalized extinction spectra of Ag-clusters, produced with different seeding gases, embedded in  $\text{SiO}_x$  and  $\text{LiF}_x$ .



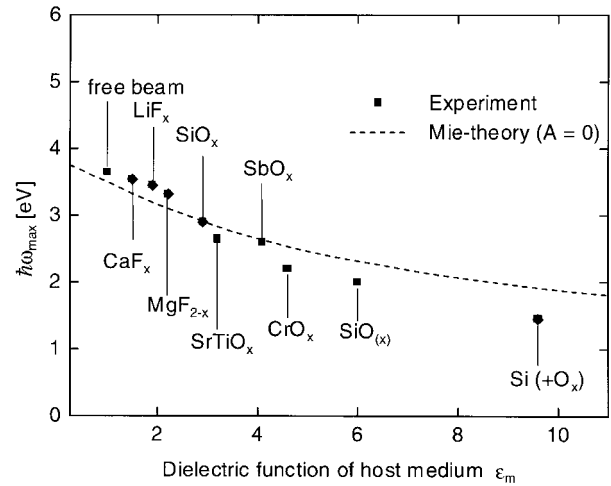
**Fig. 4.** Normalized extinction spectra of Ag-clusters embedded in various fluoride host-media (seeding gas Ar): the spectrum of the free beam is added to show “clean” clusters.

of the free cluster beam is added. In reference [3] we showed analogous results for the class of *oxides*. All volume filling factors are below 3%, so we exclude coalescence. For both classes the plasmon peak exhibits broadening and shifts which scale with the dielectric function  $\epsilon_m$  of the host.

#### Interband transitions

The low energy interband transitions of Ag are situated at  $\hbar\omega \approx 3.5$  eV. The experimental accuracy is reduced in this spectral region, as indicated by the scatter in the spectra. Beyond this limit, the spectra of Figures 1, 3 and 4 clearly show that the clusters exhibit the interband transition edge ( $4d-5sp$ ) to different amounts, being small in the free beam, somewhat more pronounced in oxides [3], and in the fluorides it is well established and similar to what is expected from larger particles.

This interesting effect will be further investigated on gold-clusters in the free beam, where the interband transition edge is situated at longer wavelengths and, hence, more precisely to be measured.



**Fig. 5.** The plasmon peak position ( $\hbar\omega_{\max}$ ) of silver-clusters ( $2R = 2$  nm) embedded in various host media: most oxidic hosts show a red shift while fluorides show a blue shift against the theoretical Mie spectra.

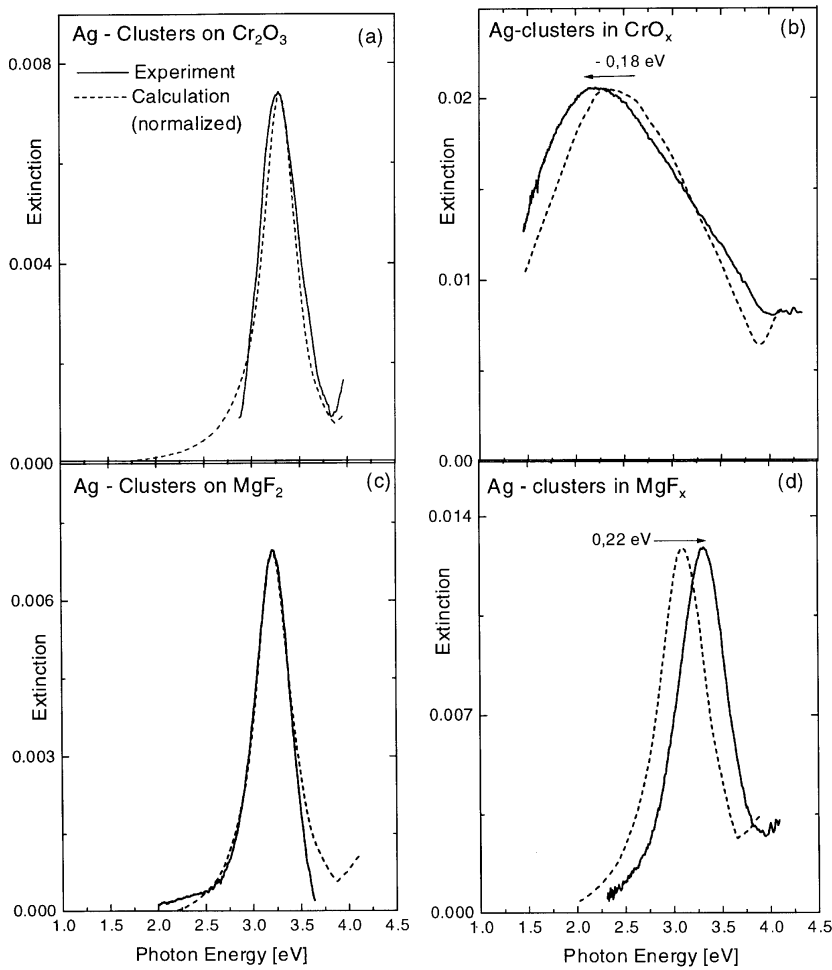
#### Mie plasmon peak

Ag clusters are known to exhibit often changes of Mie band position and width when coming into contact with foreign matter, which are beyond the predictions of Mie’s theory [2,3,9] (and literature therein). We interpreted these *additional* changes as due to *static and dynamic charge transfer* [2,3,9] in the strongly inhomogeneous interface region. Here we present new experiments on both effects and compare with previous ones.

As following from the summary of the *Mie peak positions* in Figure 5, there is a fundamental trend: while oxidic hosts mostly cause additional red shifts, compared to the prediction of Mie’s theory (which we interpreted to be due to transfer of cluster conduction electrons into the cluster/matrix interlayer) the fluorides all show different behaviour: blue shifts against these theoretical spectra, which latter only include the *dielectric shift* (by the dielectric constant of the matrix, dotted line in Fig. 5). Since, already the free clusters show (Fig. 5) a difference in the same direction (though somewhat smaller, compared to  $\text{LiF}_x$  and  $\text{CaF}_x$ ) and they are electrically neutral, we assume that the latter holds essentially also for the clusters embedded in fluorides. These results and the narrow band widths also indicate that our electron beam evaporated fluoride films are close to stoichiometry. The Mie calculations were done with the dielectric function of Ag, used in [3] which was size effect corrected. The optical properties of the matrix used were measured *in situ* from the reference position on the samples.

The most drastic effect is the *dynamic charge transfer*, reducing the Mie plasmon lifetime, to less than 10% of that of the free cluster ([2], see also Gartz *et al.* in these Proceedings), and expressing itself in according increase of resonance half width, which we describe by the previously introduced *A-parameter* [1–3,9].

Here, we present as examples two sequences of absorption spectra of the clusters deposited in Figures 6a



**Fig. 6.** Normalized extinction spectra of Ag-clusters ( $2R = 2$  nm), (a) on  $\text{Cr}_2\text{O}_3$  substrate ( $\hbar\omega_{\text{max}} = 3.27$  eV,  $A = 0.52$ ,  $a/c - 1 \leq 5\%$ ), (b) in  $\text{CrO}_x$ -matrix ( $\hbar\omega_{\text{max}} = 2.2$  eV,  $A = 3$ ), (c) on  $\text{MgF}_2$ -matrix ( $\hbar\omega_{\text{max}} = 3.21$ ,  $A = 0.55$ ,  $a/c = 0.94$ ) and (d) in  $\text{MgF}_x$ -matrix ( $\hbar\omega_{\text{max}} = 3.31$  eV,  $A = 0.83$ ).

and 6c and embedded in Figures 6b and 6d  $\text{CrO}_x$  and  $\text{MgF}_x$  respectively (where  $x$  is close to stoichiometry). The according  $A$ -parameters and the maxima of the peak positions, characterizing the dynamic and the static charge transfer effects, respectively, in the according systems are registered in the figure caption.

Summarizing, there is large broadening ( $A = 3 \pm 0.03$ ) in  $\text{CrO}_x$  and an additional red shift of  $-0.18$  eV, while the interaction in the  $\text{Ag}/\text{MgF}_x$  interface is less intense,  $A$  being only 0.83. Here, a blue shift occurs with 0.22 eV compared to the theoretical spectrum. It is interesting that in both series the effects of deposition on substrate are, roughly, the same:  $A \approx 0.6$ . As mentioned in Section 3.2, these latter spectra contain an additional parameter: the size of the contact area (where charge transfer can take place) which is determined by the surface energies. We mention [1,3] that the  $A$ -parameter was *defined* to describe the cluster size and interface induced contributions of *s*-electrons to the Mie band width. The band width itself is influenced in addition by the intraband transitions. (Hence,  $A = 0$  for clusters of bulk-like material).  $A$ -parameter values, evaluated *vice versa* from measured spectra, may contain contribution from interband excitations *provided* they are changed compared to the bulk.

As a general consequence from these investigations we conclude that clusters or, more general, nanostructural el-

ements cannot be treated as well-defined and isolated entities as long as they are in contact with some surrounding foreign medium. Instead, the proper building unit is the *cluster plus surrounding interface region*.

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