Properties of Cold Condensed Silver Chloride and of Cocondensed Silver/Silver Chloride Films

1. UV-VIS-Spectra

Helmut Gottwald, Thomas Lieser, Konrad G. Weil, and Alarieh Weiss

Institut für Physikalische Chemie der Technischen Hochschule Darmstadt

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When vapor of silver chloride is condensed with rates below 1 mm min⁻¹ onto a substrate at T = 10 K, a non-crystalline film grows. Typical of this film is the absence of the exciton absorption at 240 nm and the presence of a broad absorption extending to wavelengths > 300 nm. When the film is tempered for a few minutes at T > 170 K, it shows the typical UV-VIS-spectrum of crystalline AgCl. When silver is cocondensed with silver chloride, additional absorption around 300 nm can be observed. This situation is stable up to temperatures of T = 200 K. Then silver chloride crystallizes and silver is precipitated, leading to Mie scattering at wavelengths around 500 nm.

Condonensation of silver stabilizes the non-crystalline state with respect to deposition temperature and deposition rate. Also the transition temperature non-crystalline/crystalline is increased.

1. Introduction

In previous papers we reported on measurements of the thermodynamic functions of solutions of silver and copper in their molten halides [1, 2, 3]. The results indicated the presence of covalent species in these melts. Charge-transfer between the metal atoms and the “molecular species” leads to the stabilization of dissolved atoms in the melts. UV-VIS-spectra of the solutions showed evidence for the presence of charge-transfer-complexes [4]. Optical spectroscopy, however, of these melts does not lead to very conclusive results. The absorption edges of silver and copper chloride depend strongly on the temperature and are shifted into the visible region at temperatures close to the melting points. The spectra of the solutions, therefore, could not be resolved completely. It was especially unsatisfactory that the half width of the absorption bands could not be determined as a function of temperature.

Attempts to prepare mixtures of silver atoms with silver chloride molecules at lower temperatures, therefore, seemed justified. In this paper we report on optical properties of silver chloride layers which were condensed from the vapour onto cooled quartz windows, and on the influence of cocondensed silver on these properties.

2. Experimental

A copper block containing a fused silica window of 14 mm diameter was mounted on the cold head of a Leybold-Heraeus cryo-refrigerator R 9 1040. Using a Leybold-Heraeus temperature regulator HR 1, the temperature at the window could be adjusted between 10 and 300 K. The temperature was measured by a thermistor and a carbon resistor, which both were mounted in the copper block very close to the window. Thermal contact between the window and the copper block was optimized using indium wire.

The cold part of the refrigerator system was flanged to a vacuum system. A turbomolecular pump TPU 110 produced a limiting vacuum of 10⁻⁴ Pa. This pressure was measured at a site of the system which was at room temperature. The first stage of the refrigerator system as well as part of the second one, and the radiation shields around the copper block act as cryo pumps. The residual pressure at the fused silica window, therefore, will be far below 10⁻⁴ Pa. This can be concluded from the fact that we could not observe any water signals in the Raman spectra we obtained within a time scale of hours or days in a typical Raman experiment (see part II of this series).

Using a bellow, the whole cooling system can be fixed in two different positions. In position one, the quartz window faces two evaporation sources which...
can be heated separately. The first one was a bulb from fused silica with a small orifice at the narrow end. It contained silver chloride and was heated using a tantalum spiral. The second one was an alumina tube of 8 mm diameter with the ends of it closed with high temperature cement. It contained silver and was inserted into a molybdenum capillary which could be heated directly by electric current. An orifice in the middle of the tube allowed a molecular beam of silver to leave the source.

Between the evaporation sources and the quartz window a movable shutter was positioned. It contained a vibrating quartz balance. In a typical run, the silver source was heated until a desired deposition rate of silver was observed. Then the temperature of the silver chloride source was increased until the total growth rate of the film on the vibrating quartz monitor reached a preselected value. Finally the shutter was opened and the metal/metal halide mixture of a desired composition was evaporated onto the fused silica window. Constancy of the deposition rate \( r \) was controlled repeatedly by moving the quartz balance into the path of the molecular beams. In order to keep the angle between the two beams as small as possible, the two evaporation sources were mounted in a way that the distance between their orifices was only a few millimeters. Both sources were thermally isolated from each other by a special ceramic shield (Stenan from Rosenthal Technik AG).

To bring the system in position two, the whole cooling system, including the fused silica specimen holder, could be moved horizontally, using a bellow of 160 mm diameter. In this position, the specimen was fixed between two windows, so that UV-VIS spectra could be taken. We used a Perkin-Elmer UV-VIS spectrometer 557. This is a modular system which allows to mount the photomultiplier directly on the exit window of our specimen-containing compartment. Furthermore, it can be operated as a double wavelength spectrometer, which allows to measure the differential absorbance \( A (\lambda_2-\lambda_1) \). In the mode we used, \( \lambda_2 \) was the variable wavelength (190 nm \( \leq \lambda_2 \leq 900 \) nm), whereas \( \lambda_1 \) was fixed at 350 nm. In the figures the differential absorbance \( A \Delta A \) is shown in arbitrary units.

The whole system, as described above, is mounted on a movable chassis. With a slightly different specimen holder it can also be used to obtain Raman spectra from evaporated films as will be discussed in Part II of this series. A schematical sketch of the whole system is given in Figure 1.

3. Results

3.1. Pure Silver Chloride

Figure 2 shows the UV-VIS absorption spectra of a 100 nm silver chloride layer, condensed on fused silica at a substrate temperature of 293 K. The spectra were obtained at different sample temperatures. They are identical with spectra reported for crystalline silver chloride [5]. Figure 3 shows spectra of a film condensed at a substrate temperature of 10 K with a deposition rate of 0.3 \( \text{nm} \cdot \text{min}^{-1} \). The curve marked with “10 K” shows the absorption spectrum of the freshly prepared film. The other spectra in Fig. 3 were obtained from the same film, always at 10 K, but after annealing at the indicated temperatures for about 10 minutes.

It is clearly seen from Fig. 3 that the freshly prepared films show an absorption behaviour
Distinctly different from that of crystalline silver chloride (compare the 10 K-curve in Figure 2). The exciton absorption, which is indicative for the crystalline state [6] is completely missing in the spectrum.

Annealing at 170 K does not lead to drastic changes in the spectrum. At temperatures above 170 K, the state of the film seems to change towards a more crystalline nature. The spectrum obtained from a film which was heated at 210 K for 10 minutes is identical with that of a film condensed at room temperature.

Condensation of 100–500 nm thick silver chloride films onto substrates of 10 K with deposition rates below 0.5 nm · min⁻¹ always leads to a state which gives rise to an absorption spectrum like that marked “10 K” in Figure 3. Because of the complete absence of the exciton absorption around 240 nm, we call this the non-crystalline state of silver chloride. We could observe that the deposition rate plays an important role. At deposition rates above 1.0 nm · min⁻¹ silver chloride most frequently condenses in a crystalline state showing the exciton absorption. Only in a very few cases could we observe the non-crystalline state in films, condensed at 10 K and deposition rates > 1 nm · min⁻¹.

3.2. Silver-Silver Chloride Mixtures

3.2.1. The absorption spectrum

If one wishes to prepare atomically dispersed (matrix isolated) silver in silver chloride, the molar ratio \( n_{\text{Ag}}/n_{\text{AgCl}} \) should not exceed \( 10^{-2} \). Under these circumstances, UV-VIS-spectroscopy is not a promising technique: As we show in Fig. 3, non-crystalline silver chloride exhibits a long tail in the absorption curve, which extends into the region around \( \lambda = 300 \) nm, where atomic silver excitations are to be expected.

We, therefore, confined our experiments to conditions under which clustering of silver will take place. Most of the results described in the following are obtained with \( n_{\text{Ag}}/n_{\text{AgCl}} = 1/4 \). Series of experiments covering the region of \( 0.25 \leq n_{\text{Ag}}/n_{\text{AgCl}} \leq 0.01 \) gave only slightly different results.

The absorption spectrum of a 100 nm thick film with \( n_{\text{Ag}}/n_{\text{AgCl}} = 0.25 \) is shown in Figure 4. The curve marked “10 K” is that of the freshly prepared film. We observe again a smooth, structureless increase in absorption at \( \lambda > 300 \) nm, indicative of non-crystalline silver chloride. Additionally a broad, again structureless absorption appears above \( \lambda = 300 \) nm, extending up to \( \lambda = 600 \) nm. Subsequent heating of the film up to 200 K gives, after cooling to 10 K, no significant changes of the spectrum in this region. Only when the temperature is raised above 200 K, such changes can be seen: the low wavelength part of the spectrum indicates crystallization of the chloride (note the development of the exciton absorption), the absorption between 300 and 400 nm disappears gradually and at the same time a broad maximum centered at \( \lambda = 520 \) nm evolves.

Around \( \lambda = 300 \) nm, the absorption of the freshly prepared film is caused by silver and by silver chloride. This is confirmed by Fig. 5, which shows
of the absorption spectrum. Silver stabilizes the non-crystalline state. This stabilization not only shows up in an increase in the transition temperature but also in an increase in the maximum deposition rate, at which the non-crystalline state is formed. The films from which the spectra in Fig. 4 are taken were grown with a deposition rate of silver chloride of $3.8 \text{ nm} \cdot \text{min}^{-1}$. We, therefore, studied the influence of cocondensed silver on the formation conditions of the non-crystalline state. For this purpose, the deposition rate and the substrate temperature were changed. The results are collected in Figure 6. On the left hand side, results with pure silver chloride are presented. At substrate temperatures of 12 K and of 60 K, deposition rates of $0.5-0.6 \text{ nm} \cdot \text{min}^{-1}$ lead to films with the absorption behaviour of the non-crystalline state. At

3.2.2. Stability of the non-crystalline state

From Fig. 3 it can be seen that the non-crystalline state of pure silver chloride films becomes instable at temperatures between 170 K and 190 K. Cocondensed silver/silver chloride films can be heated up to 200 K without significant changes of the UV part of the absorption spectrum. Silver stabilizes the non-crystalline state. This stabilization not only shows up in an increase in the transition temperature but also in an increase in the maximum deposition rate, at which the non-crystalline state is formed. The films from which the spectra in Fig. 4 are taken were grown with a deposition rate of silver chloride of $3.8 \text{ nm} \cdot \text{min}^{-1}$. We, therefore, studied the influence of cocondensed silver on the formation conditions of the non-crystalline state. For this purpose, the deposition rate and the substrate temperature were changed. The results are collected in Figure 6. On the left hand side, results with pure silver chloride are presented. At substrate temperatures of 12 K and of 60 K, deposition rates of $0.5-0.6 \text{ nm} \cdot \text{min}^{-1}$ lead to films with the absorption behaviour of the non-crystalline state. At

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60 K and 3 nm \( \cdot \) min\(^{-1} \) crystallinity is indicated by the appearance of the exciton band at 240 nm. At a substrate temperature of 85 K, non-crystalline states could not be observed. The figure shows an example a deposition rate of 1.7 nm \( \cdot \) min\(^{-1} \).

On the right hand side of Fig. 6, UV-spectra of films were shown which were prepared with a deposition rate of silver chloride of 2.5 nm \( \cdot \) min\(^{-1} \), together with 10 mole percent silver. The spectrum observed with a film prepared at 12 K, is identical with that of the freshly prepared film demonstrated in Figure 4. A film prepared at a substrate temperature of 100 K shows a very similar spectrum. When the substrate during evaporation is kept at 120 K, a broad shoulder in the region around 240 nm appears, but we have to prepare our film at a temperature of at least 160 K to observe a clearly developed exciton absorption if silver is cocondensed with silver chloride. For clarity it should be mentioned that all spectra represented in Fig. 6 are taken at 10—12 K. The temperatures given in the figures are those at which the films are grown on the substrate.

4. Discussion

In this paper we attempt to show that bonding interaction occurs between non-crystalline silver chloride and silver atoms. Unfortunately, it is not possible to prove this directly, i.e. by observation of a charge-transfer-band in the absorption spectrum. Indirect conclusions in this direction, however, can be drawn from the reported results.

Experiments with cold condensed silver chloride are already reported in the literature. Rühl [7], using X-ray-techniques investigated films that were condensed on aluminum substrates at a temperature of 20 K and found them to be crystalline. Tutihasi [8] evaporated AgCl onto fused silica at 89 K and observed pronounced exciton absorption in the UV-VIS-spectrum.

These results differ from those obtained with TICl. Rühl [7] succeeded in preparing TICl films which showed liquid-like X-ray diffraction patterns by evaporation onto substrates at 20 K. The UV-VIS-spectra of these films are characterized by the complete absence of an exciton band, which is clearly developed in crystalline TICl [9].

Unfortunately, the papers of Rühl [7] and of Tutihasi [8] contain no information about the deposition rate used in their experiments. It is very likely that it was much higher than the critical rate which we report in 3.1.

The spectra we obtained with cold condensed silver chloride at low deposition rates differ from those of amorphous TICl [9] in one important feature. While with TICl the disappearance of the exciton band shifts the absorption edge to a lower wavelength, in the case of AgCl the disappearance of the exciton band is accompanied by the formation of a new broad absorption extending to wavelengths > 300 nm.

This new absorption can be explained in two different ways. One may assume that under the conditions of our experiments the film consists of a highly disordered arrangement of ions, like in molten salt. Then the undisturbed crystalline regions are too small for an exciton to be formed, but disorder-induced indirect transitions can give rise to the broad absorption around 300 nm.

On the other hand it seems possible that impinging AgCl molecules are quenched so rapidly that they cannot dissociate into ions and are condensed as molecules. In this case the absorption around 300 nm is caused by an electronic transition within a silver chloride molecule. This transition is broadened, of course, by interaction with the surroundings.

A final decision between these two models cannot be given at present. Nevertheless, we favour the molecular model, as it facilitates the understanding of the effects of the cocondensed silver.

When silver is cocondensed with silver chloride, additional absorption occurs between ~ 300 nm and 600 nm. Due to the broadness of this band, it cannot be resolved into the possible contributions of silver chloride absorption, charge transfer absorption, and plasmon excitations in small silver particles.

It is interesting that during heating of the silver containing film three phenomena occur simultaneously: disappearance of the broad absorption around 300 nm, formation of the exciton band and appearance of a broad signal in the visible region. This signal can be assigned as resulting from Mie-scattering of large silver particles (size ~ 500 nm). That means that a very fine dispersion of the metal is stabilized in the non-crystalline state, while formation of the crystalline state is accompanied by transport of silver and a drastic rise in the mean particle size.
These observations, together with the pronounced increase in stability in the non-crystalline state by cocondensed silver, are most easily explained with the assumption that silver chloride molecules are present in the non-crystalline state. At least part of the cocondensed silver then will exist in a state where it is bonded to such molecules. Dissociation of these molecules into ions would bring the silver into the very unfavourable state of a silver atom in a silver chloride crystal. So this transformation can only take place when the silver mobility is high enough to allow precipitation of the metal to occur during the transformation.

We take these observations as evidence that the postulated bonding interaction between silver atoms and silver chloride molecules does exist. Further results, derived from vibrational spectroscopy, will be published in a forthcoming paper (see Part II of this series).

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