Chapter 9

The formation of copper sulphide semiconductors inside Langmuir-Blodgett films of Cu(II) ion complexes

Summary

The fabrication of layers of copper sulphide within multilayers of copper complexes of the amphiphile 4-(10,12-pentacosadiynamidomethyl)pyridine, by diffusion of H₂S into the multilayers, was studied by UV/Vis spectroscopy. XPS measurements revealed that copper sulphides can be synthesised which differ in stoichiometry when multilayers are used which were built up from different subphases (CuCl₂ or Cu(ClO₄)₂). The distinct layer pattern of the LB films is preserved during the formation of the copper sulphide layers and the bilayer distance increases slightly by approximately 1.8 Å for the multilayers built up from a 5 mM CuCl₂ subphase, whereas for the multilayers built up from a 5 mM Cu(ClO₄)₂ subphase the bilayer spacing decreases a little by approximately 0.6 Å after the formation of copper sulphide inside these LB films. After polymerisation the multilayer structure is destroyed in the case of LB films built up from the CuCl₂ subphase, whereas the layer structure is preserved during the polymerisation process in the case of multilayers built up from a 5 mM Cu(ClO₄)₂ subphase.
Introduction

In recent years, there is a growing interest in the construction of inorganic semiconductor particles or layers in Langmuir-Blodgett (LB) films. Barraud et al. [1], recognised the possibility of the formation of metal sulphides inside LB films of behenic acid salts. In these LB films the metal sulphides were prepared by converting the metal ions into their corresponding sulphides by reaction with the gas hydrogen sulphide (H\textsubscript{2}S). So, the LB films were used as an organic matrix into which inorganic species could be inserted. On the basis of this concept several reports have been published in which metal ions (like Cd(II)) were converted to their corresponding sulphides (in this case CdS). In this way a wide variety of semiconductor nanoparticles (also called quantum dots, Q-particles, nanocrystals or clusters [2]) have been synthesised. The optical and electronic properties of semiconductor particles start to change when the diameter of the particle is reduced below the average hole-electron distance [2,3,4], the so called “quantum size effect” which could be observed as a blue shift of the band gap. This blue shift is proportional to the size (or smallness) of the particle [2-6]. All kinds of metal ions were incorporated into Langmuir monolayers [7,8] or Langmuir-Blodgett multilayers and subsequent converted with H\textsubscript{2}S, H\textsubscript{2}Se [9,10] or H\textsubscript{2}Te [9] to produce the corresponding metal sulphides, metal selenides or metal tellurides, respectively. In this way CdS [1,9,11-14], PbS [1,15,16], AgS [1], ZnS [1], NiS [1], CoS [17], PtS [18,19] and PdS [18,19] nanoparticles have been prepared. LB films containing these semiconductor particles have potential applications in optoelectronic devices as optical switches, as infrared detectors and in photovoltaics [19,20].

Barraud et al. [1,21] built up multilayers of behenic acid, incorporated Cu(II) ions into these films and exposed the multilayers to H\textsubscript{2}S. In this way Cu\textsubscript{2}S layers could be formed between the hydrophilic headgroups of the amphiphiles and they measured the electrical properties of these films and showed that these samples were also photoconductive.

From the literature [20,22,23] it is known that copper sulphide exist in a wide variety of compositions ranging from Cu\textsubscript{2}S (chalcocite) at the ‘copper rich’ side to CuS\textsubscript{2} (pyrite) on the ‘copper deficient’ side. Chen et al. [24] showed that they could influence the composition of the copper sulphide layers, formed in the LB films of copper stearate, by variation of the H\textsubscript{2}S pressure and exposure (reaction) time ranging from CuS\textsubscript{0.77} to CuS\textsubscript{1.62}.

In Chapter 3 [25] the monolayer characteristics of the amphiphile 4-(10,12-pentacosadiynamidomethyl)pyridine (Scheme 9.1) were presented upon complexation with Cu(II) ions under different conditions, like: Cu(II) ion concentration, type of counter ion, complexation time and ionic strength of the subphase. In Chapter 4 [26], multilayers of these metal complexes were built up and it was shown that the structure of these Cu(II) ion containing multilayer films could be altered by changing the counter ion (Cl\textsuperscript{-} or ClO\textsubscript{4}\textsuperscript{-}). The
amphiphile had a diacetylene functionality in the aliphatic tail, which could be polymerised upon exposure to UV light, forming a polydiacetylene with a one-dimensional, rigid, conjugated backbone [27,28].

\[
\text{CH}_3(\text{CH}_2)_{11}\text{C}≡\text{C}≡\text{C}≡(\text{CH}_2)_8\text{C}-\text{N}-\text{CH}_2
\]

Scheme 9.1

This Chapter describes the formation of copper sulphide layers within LB films of copper complexes of the amphiphile (Scheme 9.1) with \(\text{Cl}^-\) or \(\text{ClO}_4^-\) as counter ion. XPS measurements were performed in order to reveal the stoichiometry of the formed copper sulphides. The reaction with \(\text{H}_2\text{S}\) was followed by means of UV/Vis spectroscopy and the structural changes due to the copper sulphide formation were studied by small angle X-ray reflection (SAXR) measurements. Furthermore, these multilayers with copper sulphide particles were polymerised by means of UV irradiation. This polymerisation process was studied by means of UV/Vis spectroscopy and SAXR measurements.

**Experimental**

The synthesis of the amphiphile, 4-(10,12-pentacosadiynamidomethyl)pyridine and the general procedures have been outlined in the experimental sections of the Chapters 2, 3 and 4.

**Generation of copper sulphide**

The LB films were placed in a cylindrical glass cell, which was connected to a dry \(\text{N}_2\) and \(\text{H}_2\text{S}\) cylinder and disconnected from the outer atmosphere by a dressel bottle with paraffin oil. First, the glass cell was purged with \(\text{N}_2\) for 15 minutes after which \(\text{H}_2\text{S}\) was passed slowly for 15 minutes. For longer gassing times, the \(\text{H}_2\text{S}\) flow was stopped after 15 minutes and the multilayer films were left in the \(\text{H}_2\text{S}\) atmosphere for the desired time.
Results and discussion

As is already described in Chapter 4 [26], multilayers of the amphiphile can only be built up when the subphase contains Cu(II) ions. The studied multilayers consist of 16 layers of the amphiphile, built up from a 5 mM CuCl$_2$ or 5 mM Cu(ClO$_4$)$_2$ subphase at 18.7 °C and 30 mN·m$^{-1}$, by means of Z-type transfer with transfer ratios of 0.0-0.1 on the downstroke and 1.0 on the upstroke. SAXR measurements [26] revealed that the multilayers have a Y-type structure, so, the amphiphiles must have “turned over” to form the thermodynamically more favourable Y-type of structure, because the multilayers were built up with a Z-type transfer. In the Y-type structure, the Cu(II) ion rich plane is centred between the hydrophilic headgroups and upon exposure to H$_2$S this Cu(II) ion rich plane is converted into a semiconductor copper sulphide layer.

In Figure 9.1 the copper and sulphur regions of a XPS spectrum of a LB film, consisting of 16 layers of the amphiphile on silicon, built up from a 5 mM CuCl$_2$ subphase, is shown. The Cu(II) ions are indeed incorporated in the multilayers as can be seen by the presence of the copper peaks (936.5 eV, Cu 2$p_3$ and 956.5 eV, Cu 2$p_1$) (Fig. 9.1A) and their corresponding satellites which are characteristic for Cu(II) [22-24]. From the ratio between N to Cu it is concluded that the multilayers contain 1 Cu(II) ion to 3 amphiphiles [26]. Furthermore, it can be seen that no sulphur was present in the LB films (Fig. 9.1B) before exposure to H$_2$S.

After 30 minutes of exposure to the H$_2$S gas, the copper peaks shifted to lower bindings energy values (933.5 and 954.0 eV for Cu 2$p_3$ and Cu 2$p_1$, respectively) (Fig. 9.1A), the satellites disappeared and the full width at half-maximum (FWHM) became smaller. All these changes in the copper region indicated that upon exposure to H$_2$S, the Cu(II) ions are reduced to Cu(I) which is consistent with the results of Chen et al. [24]. Also Folmer et al. [22,23] concluded that no Cu(II) ions were present in copper sulphides (ranging in composition from CuS$_2$ to Cu$_2$S), but that all the copper was in the monovalent state. After the reaction with H$_2$S, the multilayers contain sulphur, as can be seen in Figure 9.1B. From the ratio Cu:S (1.05), we propose that CuS is formed in the multilayers. Upon longer gassing times, the ratio Cu:S did not change anymore. When the multilayers, built up from a Cu(ClO$_4$)$_2$ subphase, were exposed to H$_2$S, the same phenomena could be observed, again Cu(II) was reduced to Cu(I) but the stoichiometry of the formed copper sulphide layers was different. In this case, the ratio Cu:S was 0.61. Thus, in the case of multilayers built up from a Cu(ClO$_4$)$_2$ subphase, Cu$_{1.64}$S is formed. Depending on the structure of the multilayer film (which is different for multilayers built up from a Cu(II) ions containing subphase with Cl$^-$ or ClO$_4^-$ as counter ion [26]), different copper sulphides can be obtained when multilayers which
contain Cu(II) ions are exposed to H$_2$S. Furthermore, upon exposure the Cl$^-$ peaks which were present before exposure to H$_2$S for charge compensation, disappear after 30 minutes of exposure to H$_2$S, indicating that indeed all the Cu(II) ions are converted to copper(I) sulphide.

![XPS spectra](image)

**Figure 9.1:** XPS spectra of LB films, consisting of 16 layers of the amphiphile on silicon built up from a 5 mM CuCl$_2$ subphase at 18.7 °C and 30 mN·m$^{-1}$, before and after 30 minutes of exposure to H$_2$S: A, the copper region and B, the sulphur region.
Figure 9.2: UV/Vis absorption spectra of a LB film on glass, consisting of 16 layers of the amphiphile, built up from a 5mM CuCl₂ subphase at 18.7 °C and 30 mN·m⁻¹, at different times of exposure to H₂S.

Figure 9.3: UV/Vis absorption spectra of a LB film on glass, consisting of 16 layers of the amphiphile, built up from a 5 mM Cu(ClO₄)₂ subphase at 18.7 °C and 30 mN·m⁻¹: (A) 0 min. H₂S, (B) 30 min. H₂S and (C) 30 min. H₂S and 20 min. UV irradiation (254 nm).
In Figure 9.2, the absorption spectra of a LB film, consisting of 16 layers of the amphiphile, built up from a 5 mM CuCl₂ subphase, can be seen after different times of exposure to H₂S. The absorption of the formed copper sulphide layers increases at longer gassing times but after 180 minutes no further increase in absorption can be observed. This gassing time is much longer than the time needed for a maximum amount of incorporation of sulphur into the LB films, as was deduced by the XPS experiments while the XPS measurements give information about the first 50 to 100 Å at the surface of the LB film. So, the copper sulphide formation in the top layers is completed within 30 minutes while, due to diffusion, the copper sulphide formation near the substrate surface was completed after 180 minutes of exposure to H₂S. In Figure 9.2 an absorption onset of the copper sulphide layers at about 600 nm can be observed, which is in agreement with the results of Barraud et al. [21].

The absorption onset of copper sulphides strongly depends on the stoichiometry of the semiconductor. Cu₂S has an absorption onset at about 1050 nm [29]. The exact position of the absorption onset depends on the method of preparation of copper sulphide films. When the copper content of the copper sulphides is lowered the absorption onset shifts to lower wavenumbers. For instance, Cu₁.₈S and copper sulphides which are more copper deficient have an absorption onset at about 600 nm [29-31]. Therefore the found absorption onset at approximately 600 nm already indicates that the formed copper sulphide inside the LB films of the copper complex is not Cu₂S but is more copper deficient. Furthermore, absorption spectra of copper sulphide nanoparticles show a sharp blue shifted peak [32,33]. Therefore it can be assumed that the formed copper sulphides in the LB films are arranged as layers between the hydrophilic headgroups of the amphiphilic ligands because an absorption onset at about 600 nm is found and no sharp absorption peak is observed.

In Figure 9.3 the absorption spectra of a LB film on glass, built up from a 5 mM Cu(ClO₄)₂ subphase, before and after 30 minutes of exposure to H₂S can be seen. Moreover, the absorption of the formed copper sulphide layers did not increase anymore after 30 minutes of exposure to H₂S. Apparently the H₂S gas diffuses much faster into multilayer films built up from a 5 mM Cu(ClO₄)₂ than in the case of LB films built up from a CuCl₂ subphase. This phenomena is in agreement with the results from Chapter 4 [26], in which was concluded (from the much faster reduction of the Cu(II) ions to Cu(I) ions inside LB films built up from 5 mM Cu(ClO₄)₂ subphase, due to the soft X-rays in the XPS apparatus) that the LB films built up from a 5 mM Cu(ClO₄)₂ subphase have a more open structure than multilayer films built up from a CuCl₂ subphase.
Figure 9.4: Small angle X-ray reflection curves of a LB film on silicon, consisting of 16 layers of the amphiphile built up from a 5 mM CuCl$_2$ subphase at 18.7 °C and 30 mN·m$^{-1}$, at different times of exposure to H$_2$S.

Figure 9.5: Small angle X-ray reflection curves of a LB film on silicon, consisting of 16 layers of the amphiphile built up from a 5 mM Cu(ClO$_4$)$_2$ subphase at 18.7 °C and 30 mN·m$^{-1}$: (A) 0 min. H$_2$S, (B) 30 min. H$_2$S and (C) 30 min. H$_2$S and 20 min. UV irradiation.
Figure 9.4 shows the SAXR measurements of a multilayer film, consisting of 16 layers of the amphiphile on silicon, built up from a 5 mM CuCl₂ subphase, at different times of exposure to H₂S. The multilayer film has a regular layer pattern with a bilayer spacing of 60.0 Å as can be calculated from the positions of the Bragg peaks. After 180 minutes of exposure to H₂S, the second Bragg peak disappears and the first and third Bragg peak shift to slightly lower reflection angles, indicating an increase in bilayer distance after formation of the copper sulphide layers. The multilayer now has a bilayer spacing of 61.8 Å. Thus, upon formation of the copper sulphide layers the bilayer distance increases 1.8 Å. From the disappearance of the second Bragg peak can be concluded that the even harmonics make no contribution to the electron density profile, which was also found by Facci et al. [11], who claimed that the disappearance of the even peaks is consistent with the marked decrease in electron density in the middle of the bilayer planes upon formation of the metal sulphide particles.

In Figure 9.5 the SAXR measurements of a multilayer film consisting of 16 layers of the amphiphile from a 5 mM Cu(ClO₄)₂ subphase on silicon, before and after 30 minutes of exposure to H₂S, can be seen. The Bragg peaks have shifted slightly to higher scattering angles indicating that the bilayer spacing has decreased upon exposure to the reducing gas. After exposure to H₂S the bilayer is 58.6 Å. Thus, upon exposure to H₂S the bilayer spacing has decreased with 0.6 Å. Probably the formation of the copper sulphide layers induces a slightly different packing of the aliphatic tails in such a way that the aliphatic tails make a larger tilt angle with respect to the surface normal. This phenomena was also found by Luo et al. [17] for cobalt stearate multilayer film. They found that after exposure to H₂S, the bilayer spacing of the LB films decreased from about 50 Å to 40 Å, in this case the hexagonal packing of the amphiphiles was transformed into an orthorhombic one, due to exposure to H₂S.

The multilayer films can easily be polymerised by exposure to UV light (λ = 254 nm) under argon atmosphere. However, the regular layer structure of the LB film built up from a CuCl₂ subphase is completely destroyed, as has already been described in Chapter 4 [26], for LB films which were not exposed to H₂S. Figure 9.3 shows the UV/Vis spectral changes of a multilayer film, consisting of 16 layers of the amphiphile on glass, built up from a 5 mM Cu(ClO₄)₂ subphase after 20 minutes of exposure to UV light. The red form of the polymer with λ_max = 540 nm is formed and after 20 minutes no further increase in absorption could be observed, indicating that the maximum degree of polymerisation is reached after 20 minutes of exposure to UV light which was also the case for multilayers built up from a 5 mM Cu(ClO₄)₂ which were not treated with H₂S [26]. From the SAXR measurement of Figure 9.5 it can be seen that the layer structure of a LB film built up from a 5 mM Cu(ClO₄)₂ subphase
after the H$_2$S treatment is preserved during the polymerisation process, although the bilayer distance decreases from 58.6 Å till 56.6 Å upon exposure to UV light. This decrease in layer thickness is probably caused by a conversion of the all-trans alkyl chain into a more irregular one containing gauche conformations during the polymerisation process, as has already been pointed out in Chapter 4 [26] by means of FT-IR measurements.

Conclusions

It has been shown that it is possible to fabricate semiconductive copper sulphide layers between planes of hydrophilic headgroups of amphiphilic ligands in a LB film without disturbing the regular layer structure. XPS measurements showed that Cu(II) ion containing multilayers, with different counter ions (ClO$_4^-$ or Cl$^-$) can produce copper sulphide layers which differ in stoichiometry. The formation of copper sulphide can nicely be followed by UV/Vis spectroscopy. Furthermore, the layer structure of the LB film is completely destroyed when the LB film (containing Cl$^-$ as anion) is exposed to UV light, whereas in the case of multilayers with ClO$_4^-$ as counter ion, the layer structure is preserved during the polymerisation process.

References

The formation of copper sulphide inside Cu(II) ion containing multilayers