

ON THE CONTRASTING EFFECT EXERTED BY A THIN LAYER OF CdS AGAINST THE PASSIVATION OF METAL ELECTRODES COATED WITH THIOLS

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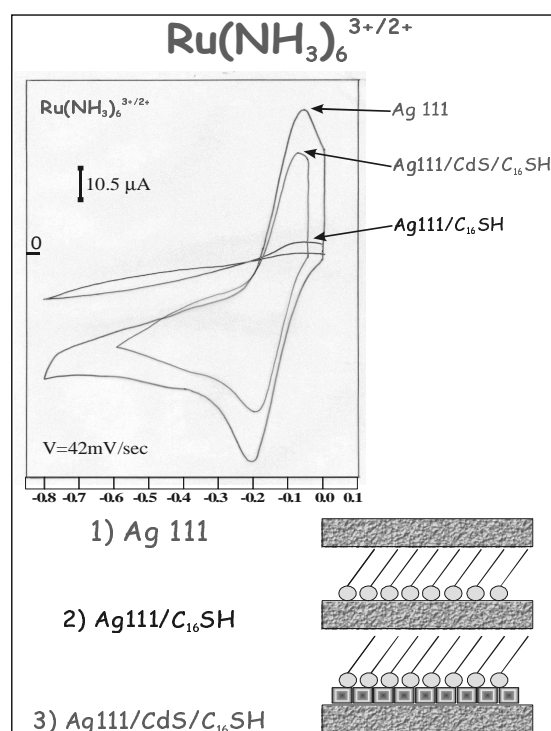
The passivation of metal electrodes covered by self-assembled monolayers of thiols is well known. The disappearance of the voltammetric peak of redox species in solution is a classical test for the formation of full layers of thiols. The assembly of organic layers on metals has been the focus of numerous studies in recent years. Similar studies on semiconductors are still very limited. However, self assembled monolayers on semiconducting surfaces seem to exhibit different properties [1]. Among them, the possibility of a higher tunneling effect with the resulting effect of a possible electron transfer through self assembled monolayers films. Therefore, self assembly on semiconductors could become interesting whenever a charge transfer is required. As an example, they could be used to anchor molecules that change their properties following an electrochemical reduction or oxidation.

Our group has a great experience in the growth of II-VI and III-V compound semiconductors on silver single crystals by the Electrochemical Atomic Layer Epitaxy (ECALE) method [2]. This is a method based on surface limited phenomena such as underpotential depositions. In the ECALE method, the upd of the metallic element is alternated with that of the non-metallic element to form a single monolayer of the compound per cycle. The number of cycles determines how thick the deposit will be. The characteristics of composition, morphology and structure of the compounds grown by ECALE, as well as the bandgap values determined by photoelectrochemical measurements, indicate the high quality of these compounds [3,4]. Therefore, we used silver surfaces covered by an ultrathin layer of CdS as substrate for self assembling of n-hexadecanethiol ($C_{16}SH$), and we compared the experimental results with those obtained by using the bare silver surface as substrate.

Hexaaminerutenium ion used as a redox probe confirmed the expected behavior. The strong insulating effect of $C_{16}SH$ deposited on Ag(111) is shown by the inhibition of the voltammetric peak of $Ru(NH_3)_6^{3+/2+}$. On the contrary, the voltammogram obtained on CdS covered Ag(111) is very similar to that obtained on the bare Ag(111) electrode. Side experiments showed that the $C_{16}SH$ forms a monolayer on Ag(111)/CdS.

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