1. Introduction and objectives

- By 2050, the world population will increase by 34%, meaning that food production must increase by 70% [1].
- Precision agriculture is a method to optimize crops. These systems are highly automated and require the use of a variety of sensors to detect CO₂, humidity, pH to name a few. pH detection remains a non-trivial task requiring frequent calibration of expensive pH-meters.
- Past simulations [2] on Cu-IllSIs predicted appearance of new metastable defect levels close to the conduction band under light stimulation, due to chalcogen vacancies. For extensive use in precision agriculture, cheaper and easy-to-manufacture sensors would be an asset. Sb₂S₃ and Sb₂Se₃ are semiconductors with suitable band gaps for visible light absorption (approx. 1.8 [3] and 1.1 eV [3,4] for crystalline phase) and are easily synthesized as thin films by chemical bath deposition. Photoconductivity could be correlated to the concentration of chemicals in a liquid in contact with the film via redox reactions.

Objectives

- Vary the chalcogen precursor concentration during deposition to explore the range of photoresponsiveness of chalcogen-rich-deficient films
- Design a device for measurements of photoconductivity in aqueous media
- Test Sb₂S₃ and Sb₂Se₃ films at different pH

2. Chemical bath deposition [4]

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<tr>
<th>Sb₂S₃</th>
<th>Sb₂Se₃</th>
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<tr>
<td>1. Microscopic slides cleaning in ultrasons and detergents</td>
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<td>2. Deposition of polydopamine (PD) by precipitation for 30 min at pH 8.5 [5]</td>
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<td>3. Deposition, by precipitation, for 2 hr at 10°C</td>
<td>3. Deposition, by precipitation, for 2 hr at approx. 24°C</td>
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<td>4. Annealing: for 1 hr at 300°C and 2 Torr of N₂, to obtain crystalline phase</td>
<td>4. Annealing: 30min at 300°C and 2 Torr of N₂, with 50 mg of powdered 5% etched, to obtain crystalline phase</td>
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3. Experimental set-up

The device for photo-electrical measurement in aqueous media is composed by three parts (a), (b). a, the main body, in HDPE (c), with the analyte chamber (d). 2. The O-ring in soft Teflon. 3. The aluminum cover.

The slide, with the thin film towards the analyte chamber, is clamped between the main body and the cover thanks to brass screws and nuts, sealing the chamber.

4. Results

The glancing incidence X-ray diffraction patterns demonstrate deposition of crystalline (a) Sb₂S₃ on PD seed layer and (b) Sb₂Se₃ + SeO₃ on bare glass.

(c) Typical photoresponse of Sb₂S₃ and Sb₂Se₃ thin films, approximately 150 and 120 nm thick respectively, on bare glass. Crystalline samples are 2 orders of magnitude more photo-sensitive (R-dark/R-light ratio) than amorphous ones, Sb₂S₃ has the highest photo-sensitivity, almost 10⁴, making it the best candidate for sensing purposes. They have a resistivity in the order of 10⁻²Ω·cm. (d) Typical photoresponse of bare PD and Sb₂S₃ films on PD. PD shows a resistance in the order of 10³Ω·cm. It shows that amorphous films in dark and light and crystalline samples in dark condition, as shown from the black dashed line in image (c). Crystalline Sb₂S₃ is more suited for measurements in aqueous media, because it shows a lower R-light than PD.

For Sb₂Se₃, the concentration of the chalcogen precursor (sodium thiosulfate) was varied between 0.2 and 1.8 M in steps of 0.2 M. Non-filmal (1M) samples were not always stable due to film fragility. Figure (e) shows that chalcogen deficiency in crystalline samples did not produce order of magnitude changes in the photoresponse in terms of light and dark resistance, thus photoconductivity. The same observations are valid for Sb₂Se₃, where the selenosulfate concentration was diminished from the saturation limit for Selenium (0.4 M) to 0.1M, figure (f). There are no reasons for chalcogen’s tuning. Electron microscope analysis revealed Sb₂Se₃ chalcogen atomic ratios of approx. 1:1.5 instead of 1:1.3, hence the films are already chalcogen deficient. Precursor’s concentration variation produced films with little change in these ratios, in the order of few percents.

(m) Each curve represents a crystalline Sb₂S₃ sample on PD that was exposed to the three different pH. Cycles of 60s of dark, 60s of light and 60s of dark were performed. The average light-resistance detected by the electrometer at constant geometry decreases monotonically when pH increases, in all cases, except for the green sample at low pH.

5. Conclusion

- Variations in the concentration of the chalcogen precursor during deposition does not produce appreciable “order-of-magnitude” changes in the photoresponse of Sb₂S₃ and Sb₂Se₃.
- Bio-inspired polypolamine seed-layer increases the adherence of Sb₂S₃ thin films on glass and extends life under water at neutral pH. We observe contrasting effects on Sb₂Se₃, the reason why it was not tested for pH detection.
- A prototype for testing photocatalysis in aqueous media was designed and successfully tested on Sb₂S₃ samples.
- We observe that resistance under illumination at constant geometry decreases when the pH increases on Sb₂S₃ thin films.
- Figures (n) and (o) show that the resistivity of the electrolyte, mainly linked to the salt content, and water splitting occurring at the anodic/cathodic regions of the film could influence the measurements. The presence of Red₂⁺ reactions involving H⁺OH⁻, thus pH, is not proven and needs to be verified.

6. Outlook

- Test salty solutions with different resistivity and same pH to verify the influence of R-electrolyte, eventually observe for evolution of bubbles (if possible).
- Broaden the research on polypolamine: morphology, optical and electrical properties. Test other substrates such as Lb₂S₃, CDS (show persistent conductivity), test other substrates that are more resistive than polypilamine.

References

4. Prof. Anna Fontcuberta-Morral 1 Project supervisor, Department of Materials Science ad Engineering, JMSC, EPFL.
2. Prof. Rafael Jaramillo, Department of Materials Science ad Engineering, JMSC, EPFL.

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