High Accuracy printed electronics down to µm size, for Organic Large Area Electronics (OLAE) Thin Film Transistor (TFT) and Display Applications

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[1] https://cordis.europa.eu/project/id/646296
[2] https://cordis.europa.eu/project/id/646155/de
[3] https://cordis.europa.eu/project/id/814401/
[4] https://www.nanosafetycluster.eu/

2 DOCUMENT CONTROL

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3 EXECUTIVE SUMMARY

In this document, we present a safety evaluation of barrier materials, which play a crucial role in protecting the active layer materials of printed electronics from moisture and oxygen. These barrier materials are remarkably thin, typically only a few tens of nanometres thick. Our focus in this project has been primarily on metal oxides, which are commonly used for this purpose.

There are various coating technologies available for the production of barrier materials, and within this report, we assess two of them that have been utilized in our project: Atomic Layer Deposition (ALD) and Electrostatic Spray Assisted Vapor Deposition (ESAVD) along with its variations.

ALD is typically carried out in an enclosed environment, effectively minimizing worker exposure to any generated nanomaterials. However, this method has its drawbacks, such as high energy consumption and the generation of chemical waste (unused precursors). Additionally, it requires highly reactive precursors and can produce toxic by-products during the process.

On the other hand, ESAVD offers a promising alternative to ALD, characterised by lower energy consumption and the potential use of safer chemical precursors. To ensure worker safety when working with this coating technology, it is crucial to operate it in an enclosed environment. With appropriate ventilation in place, we anticipate that worker exposure to nanomaterials will remain low.

In summary, our safety evaluation underscores the importance of selecting the most suitable coating method for barrier materials, considering both worker safety and environmental sustainability. The choice between ALD and ESAVD should be made with a clear understanding of the associated risks and benefits, ultimately contributing to the safer and more sustainable development of printed electronics.

4 CONTENTS

5 INTRODUCTION

Electronics displays based on technologies like OLED (organic light emitting diode) and QD-OLED (quantum dot), are highly susceptible to moisture and oxygen. An efficient encapsulation of the active layers is vital to ensure a long lifespan of the devices they are incorporated into. For traditional OLEDs the encapsulation is done with glass or metal which is sealed and fixated in space with the help of a resin. However, this method is not always applicable to flexible organic electronics. For these substrates other ways of encapsulation, for example, based on thin layers, are used. In the HI-ACCURACY project, different materials and coating techniques for the production of such thin films (barrier materials) were investigated.

Commonly employed barrier materials include metal oxides such as aluminium oxide and titanium oxide. Within the scope of this project, we explored two coating techniques: Atomic Layer Deposition (ALD) and Electrostatic Spray Assisted Vapor Deposition (ESAVD). This report provides an overview of the fundamental operational principles of both techniques, followed by an assessment of their safety and sustainability. Our focus here does not specifically hone in on the barrier materials themselves, as safety concerns are more closely tied to the deposition methods employed rather than the chemical composition of the materials. However, we have selected literature examples that align with the barrier materials utilised in the project.

6 SAFETY ASSESSMENT OF BARRIER MATERIALS

6.1 COATING TECHNIQUES

Atomic Layer Deposition (ALD) is one of most used deposition techniques. It is based on a vapor phase coating, and allows to form uniform layers which achieve an excellent thickness control. Also challenging substrates, such as structures with a high-aspect-ratio, can be coated. The working principle of ALD is summarized in Figure 1.

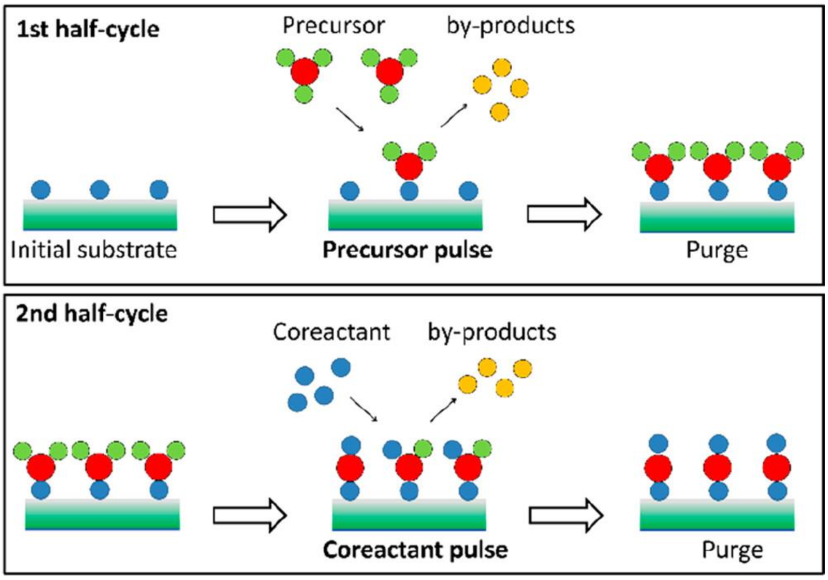

Figure 1: Working principle of Atomic Layer Deposition (ALD). Reproduced from Weber et al. (1) according to CC BY-NC-ND 4.0 licence.

The functional groups on the substrate react with precursor molecules, which are in gaseous form. The unreacted precursor molecules and by-products are then purged from the reaction chamber (1st half-cycle). This is followed by a second reactant and another purge of by-products and unreacted second reagent (finishing 2nd half cycle). Repeating this cycle leads to layer-by-layer formation of thin films (nanofilms). An example of typically used volatile reagents to produce aluminium oxide barrier layers are trimethylaluminium and water; to produce TiO_2 – titanium tetrachloride and water.

ALD process has some drawbacks (vide infra), thus, within the HI-ACCURACY project also alternative coating techniques were investigated, naming, Electrostatic Spray Assisted Vapour Deposition (ESAVD). This method uses aerosol assisted chemical vapor deposition technique (Figure 2).

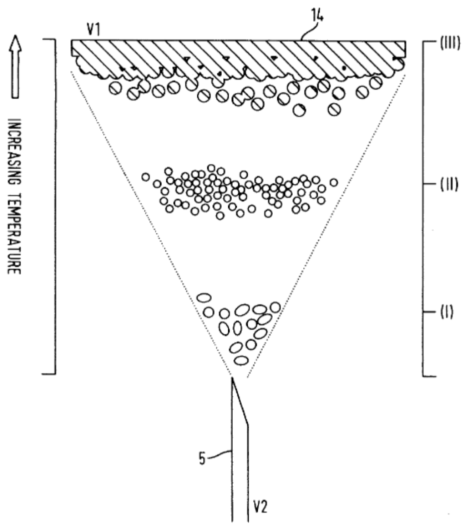

Figure 2: Working principle of electrostatic spray assisted vapour deposition (ESAVD). Figure taken from patent US 6,331,330 B1.(2) Substrate is shown on the top.

The atomised aerosol precursor is sprayed from the nozzle (number 5 and (I) in Figure 2) across an electric field. The temperature increases as the atomised particles are moving towards the substrate, leading to a rapid evaporation of the solvent. The chemical precursor subsequently undergoes either decomposition, or (and) a chemical reaction. Ultrafine particles of the target compound are produced, which are then deposited on the substrate. Advantage of this method is its higher atom economy (less precursor solution is wasted) and no need for a vacuum.

6.2 IMPLEMENTATION OF ALD PROCESS IN FRAUNHOFER IAP

A safety assessment of ALD process was performed during an on-site company visit at Fraunhofer IAP. To coat the active layers with barrier materials, the substrates are placed in a glove box (Figure 3a).

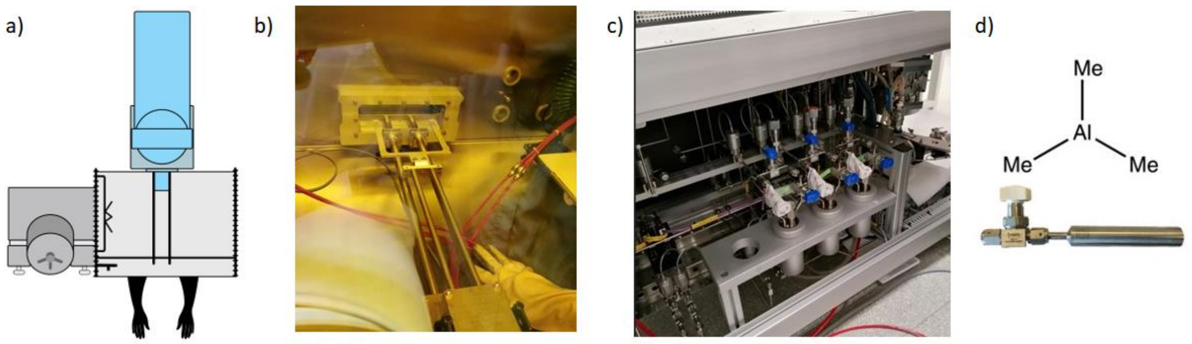

Figure 3: a) Scheme of ALD setup in Fraunhofer IAP, on the left side airlock chamber can be seen, blue – ALD device; b) photo of sample stage; c) photo of reagent supply; d) example of a storage cylinder for trimethylaluminium, image taken from Strem Chemicals, Inc. product catalogue.

The glove box is located in a cleanroom; thus, a personal protective equipment is used at any given time (overall, gloves, respiratory face masks). The substrate is placed on a sample stage inside a glovebox and moved into vacuum chamber (Figure 3b). The ALD process is automatised and the worker does not have to perform any chemical reactions personally, making exposure to hazardous chemicals highly unlikely. Precursor solutions, such as trimethylaluminium, are safely enclosed in metal cylinders (Figure 3c-d). Filling of the precursor containers is performed in the glovebox, so that direct contact is impossible and con only occur in case of an accident with exchange of the atmosphere inside and outside of the glovebox (e.g., damage of the gloves which would allow that precursor would be transferred through the leak).

The likeness of workers exposure to hazardous chemicals is low, especially since the processes are closed. However, an appropriate exhaust system is vital, as during ALD process, chemical gases are produced as a by-product, and also unreacted precursors needs to be purged (see also, Figure 1). Overall, the ALD method can be considered as safe.

6.3 SUSTAINABILITY AND SAFETY OF THE COATING TECHNIQUES

Studies of ALD environmental impact have found, that this method can have a very large precursor and energy waste. Thus, the environmental impact is the highest in the category of fossil fuels use. For the generation of Al_2O_3, material use efficiency in ALD process has been found to be below 20%. Also, emission of greenhouse effect gases (methane, ethane) as well as nanoparticles is known to happen while making Al_2O_3. In case of TiO_2 layers, the material utilisation efficiency is even lover, below 1%. The analysed process itself happened at 90°C temperature (the precursor temperature is kept at room temperature) and under 500 Pa pressure, demonstrating the high energy demand (with the overall energy efficiency being very low). At the same time, processes can be optimised, thereby lowering the environmental impact (for example, by adjusting the reactor design). ALD requires highly reactive precursors, which means that many of the used chemicals are hazardous. Simultaneously, developing of less reactive precursors can lead to the need of harsher reaction conditions. Nevertheless, development of alternative, less energy demanding ALD modifications, is possible. For more information, please see assessment for the environmental impact of ALD (and how to lower it) by Weber et al. and references therein (1).

To the best of our knowledge, there are no studies providing sustainability analysis or life cycle assessment of Electrostatic Spray Assisted Vapour Deposition (ESAVD). The precursors used in this method can be environmentally more friendly and are used more efficiently in comparison to, for example, ALD, which provides a clear environmental and safety advantage. Furthermore, ESAVD is performed in ambient pressure and in case of compounds which are not sensitive to O_2 (such as, Al_2O_3), also in open atmosphere (3).

Choy has used titanium diisopropoxide bis(2,4-pentanedionate) in 2-propanol (isopropanol) as precursor for the deposition of TiO_2 layer using ESAVD (using polyethylene glycol as an additive). The deposition temperature was varied from 350-500°C and nanocrystalline TiO_2 film formation could be achieved (4). Since the nanomaterial formation reaction happens during the coating process (see Figure 2 and the description text following), workers exposure is unlikely. However, there is a general lack of exposure studies investigating worker exposure to spray deposition coatings in a research laboratory setting. But a reasonable comparison can be done with the results published by Bellagamba et al. (5). In this study, a spray-casting of graphene nanoplatelets was performed. Each deposition lasted 3 seconds, and two different nozzles were used. One with a diameter of 0.8 ("first spray") and second with 1.2 mm ("second spray"), a comparable size to the diameter used for electrostatic deposition (6). The spray deposition was performed in a ventilated fume hood (equipped with a modular filtration column with HEPA filters GF4AS, with a maximum flow rate of 460 m^3/g, and inside air velocity > 2 m/s). A schematic representation of the laboratory and the sampling points are given in the Figure 4a.

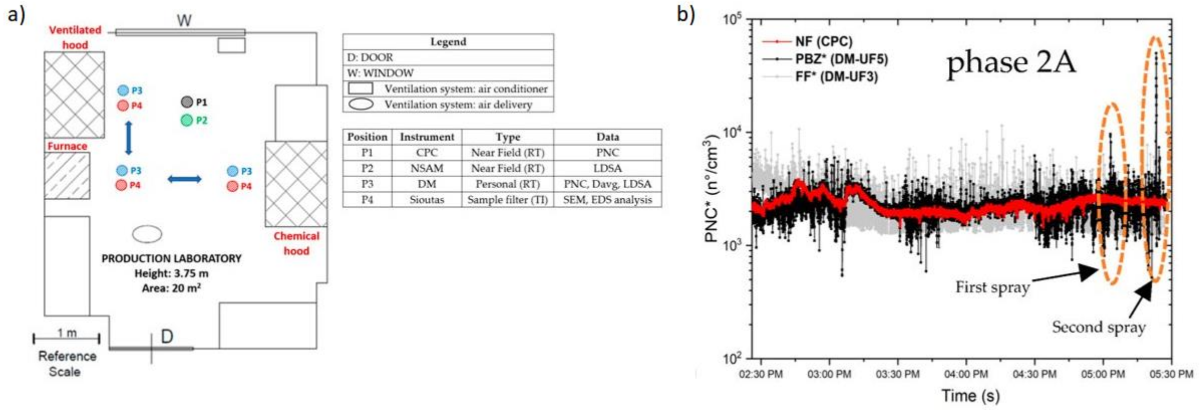

Figure 4: a) Scheme of the production laboratory b) PNC - particle number concentration: NF – near field; PBZ - personal breathing zone, i.e., within a 0.3 m radius of worker's nose and mouth; FF – far field (another laboratory where no work with nanoparticles is performed). Adopted from Bellagamba et al. (5) according to CC BY 4.0 Deed licence.

The worker who was performing the spraying was equipped with a personal impactor (attached to the lab coat), measuring particle number concentration (PNC) in the personal breathing zone (PBZ, within 0.3 m radius of the worker's face). Results indicated that during the spray coating processes a local maximum of PNC could be detected in workers PBZ. At the same time, no PNC increase was found in the near field location (Figure 4b). Authors concluded that there is potential to local nanoparticle increase during the spray coating process near the operator who performs the task. Efficient ventilation system prevents those nanoparticles from escaping into the laboratory environment and also limits the workers exposure time. The final recommendation of this study was to perform spray coating in an enclosed system (e.g., glove box) or by introducing a remotely controlled spraying device (5).

Suspensions can also be used for the aerosol assisted electrospray deposition. For example, Jaworek et al. used the setup shown in Figure 5 to deposit TiO_2, ZnO, MgO and Al_2O_3 nanoparticles (7). The solutions were prepared by stirring commercially available nanoparticle powders in methanol and ethylene glycol mixtures. The coating was done with a small suspension flow (1-1.5 ml/h), over a period of 30-60 minutes.

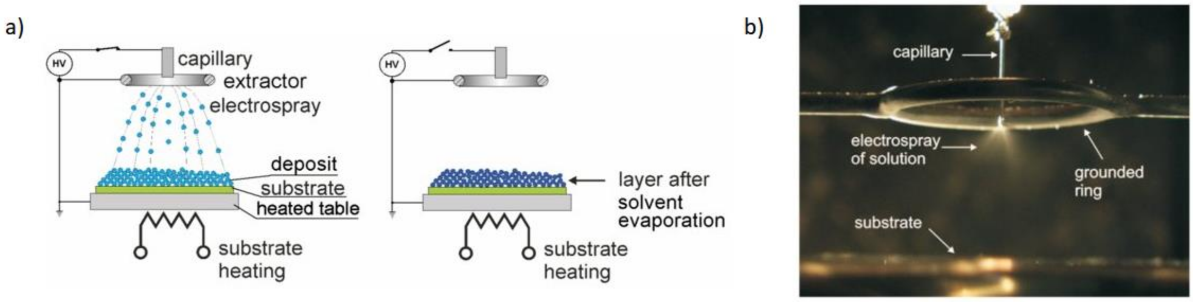

Figure 5: a) Scheme of an electrospray system for deposition using suspensions b) photo of setup in laboratory, the inner diameter of the grounded ring is 30 mm. Adopted from Jaworek et al. (7) according to CC BY 4.0 Deed licence.

Considering the exposure measurements described by Bellagamba et al., it can be expected that operating of such a low-energy electrospray system as described by Jaworek et al. would not lead to serious exposure to nanomaterials (if the process is performed in well-ventilated fume hood or enclosed environment). A larger possibility of worker exposure to nanoparticles in this case arises from weighting of the materials during the preparation of nanomaterial suspensions (8). For more detailed discussion about the exposure to nanomaterials during various handling operations in the laboratory, the reader is referred to the deliverable report D2.5 "Nanosafety assessment of conductors, dielectrics and OSCs".

For some materials it is also possible to avoid solid nonmaterial handling altogether by taking advantage of the sol-gel process to produce nanosized metal oxides. For example, Chen et al. prepared ZnO nanoparticles by aging 0.05M zinc acetate dihydrate in ethanol solution under ambient conditions. The obtained solution was used for electrospray coating of an aluminium plate (6). A further advantage of using suspensions is that for the coating process there is no need to reach high temperature (to promote a chemical reactions in vapor phase). Instead, the substrate is heated only to ensure a complete evaporation of the used solvent (sintering can be applied to the coated layer if necessary) (9).

In conclusion, ESAVD as an alternative coating technology to ALD has a promise as a more sustainable and safe method to produce barrier materials. At the same time, potentially it has a larger possibility of worker exposure to nanomaterials, thus, careful selection of the precursors as well as well-designed work place must be implemented.

6.4 EXPOSURE TO BARRIER MATERIALS AT THE END-OF-LIFE OF ELECTRONICS

The analysis of coating processes suggests that laboratory workers are exposed to minimal levels of nanoparticles during the production of barrier materials. The likelihood of end-users, i.e., consumers of electronics containing these materials, being exposed is even lower due to the fixed form of nanomaterials in electronic devices (10). However, when it comes to the end-of-life phase of electronics, the primary goal should be recycling of these products, particularly given that electronic waste contains a significantly higher metal content than metal ores (11).

The electronic waste recycling process typically includes several key steps: collection, dismantling, pre-processing, and final metal recovery. It is during the dismantling phase that workers may face potential exposure to various materials present in electronics (12, 13). Therefore, in the development of barrier materials for printed electronics, researchers are strongly encouraged to choose chemicals that are both safe and sustainable, with a particular emphasis on avoiding heavy metals.

7 CONCLUSIONS

Atomic Layer Deposition (ALD) stands out as one of the safest coating techniques, particularly when considering worker exposure to nanomaterials during the production of barrier materials in printed electronics. However, alternative methods, such as Electrostatic Spray Assisted Vapor Deposition (ESAVD), can also offer a high degree of safety when operated under appropriate conditions, such as, within well-ventilated and enclosed fume hoods.

ESAVD is a promising choice for coating techniques, offering enhanced safety and sustainability benefits. Notably, ESAVD employs less reactive chemical precursors, mitigating potential safety hazards often associated with other deposition methods (such as ALD). Furthermore, its lower energy demand aligns with sustainability goals, making it a compelling option for various applications. However, the technique needs to be assessed in terms of technical feasibility and envisaged performance parameters too.

There is a notable gap in research concerning the exposure of laboratory workers in small-scale research and development laboratories that employ chemical vapor deposition techniques, such as electrostatic spray coating, to nanomaterials.

8 RECOMMENDATIONS

- If Atomic Layer Deposition (ALD) is the preferred method for coating, it is recommended to undertake an optimization process for reactor parameters, precursors, and other relevant variables. Such optimisation should aim to enhance the safety and sustainability of the ALD process. In this regard, the assessment conducted by Weber et al. (1) can serve as a valuable source of information and guidance.

- Encouragement is extended for the development of alternative coating methods, particularly those that exhibit the potential to provide enhanced safety and sustainability. Such methods should prioritize minimising worker exposure to nanoparticles and employ non-hazardous chemical precursors.

- Given the existing dearth of data from small-scale laboratories engaged in the spray coating of small substrates, we strongly recommend conducting comprehensive exposure studies in these settings and subsequently publishing of the acquired data.

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