World Journal of Chemical Education, 2021, Vol. 9, No. 4, 104-110
Available online at http://pubs.sciepub.com/wjce/9/4/2
Published by Science and Education Publishing
DOI:10.12691/wjce-9-4-2

Hello Future! Printed Electronics as a Hands-On Experiment for Science Teaching

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Received October 11, 2021; Revised November 12, 2021; Accepted November 28, 2021

Abstract Printed electronics is an emerging research field and is going to play a vital role in our everyday-life in the near future. Luminescent printed electronic devices can be very thin and flexible, which makes them feasible for new applications. Such EL-devices are already being applied in automobiles. For the school-implementation of printed electronics the authors have developed a flexible EL-device, which can be hand-printed using low-cost materials and methods.

Keywords: *printed electronics, electroluminescence, semiconductor, hands-on experiment*

Cite This Article: Lena Halbrügge, Amitabh Banerji, and Sven Rösler, “Hello Future! Printed Electronics as a Hands-On Experiment for Science Teaching.” *World Journal of Chemical Education*, vol. 9, no. 4 (2021): 104-110. doi: 10.12691/wjce-9-4-2.

1. Introduction

Electronic devices, which are partially or completely fabricated via printing processes, can be referred to as printed electronics [1]. This technology is increasingly introduced into different parts of our every-day life. Not only batteries but also antennas and devices for the use in medical technology can be printed today. Especially, the automotive industry uses several printed electronic devices, e.g. touch-screens or -sensors [1]. Furthermore, light emitting devices such as safety lightnings and self-illuminating tachograph-discs can be produced by printing methods as well. Printed electronic devices are very thin and flexible and can be embedded into a wide spread of applications [1]. Due to this feature new fields of application have become accessible, especially tiny and light weight components like RFID-chips (radio frequency identification) [2]. Moreover, the possibility of roll-2-roll fabrication of electronic devices is economically attractive which makes the technology very promising for the future.

To prepare students for a life in an increasingly technology-dominated world and to motivate them for STEM (science, technology, engineering, mathematics) it is crucial to implement future technologies into the science curriculum of schools and universities. Our group has developed an experiment to hand-print an EL-(electroluminescence) device and to teach semiconductors on an undergraduate level. The following article presents the hands-on experiment along with the relevant theoretical backgrounds of printed electronics and EL-devices.

2. Machine-based Screen-printed Electro-Luminescent Device

When it comes to the printing of electronics there are different aspects that need to be considered. For better understanding, a printed electronic device (i.e. an electroluminescent foil) can be imagined as a “high-tech sandwich”, which is composed of different active layers stacked on each other (Figure 1).

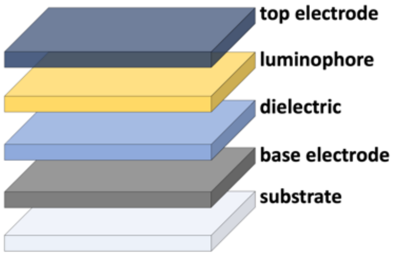

Figure 1. Scheme of a printed electroluminescent device

A thin flexible substrate builds the foundation on which all other layers are printed step by step. For the printing process itself, it is crucial that the materials are provided as inks. These inks can differ as well as the substrate [3]. There can be identified three different properties of “electronic inks”, such as conducting, semiconducting and dielectric ones. The substrates can be made of paper, PET, glass, textiles or other suitable materials. There are several printing techniques, which all can be either assigned to mask-based or mask-less methods. Mask-less printing methods are inkjet and aerosol-jet printing, whereas mask-based printing can be flexographic, gravure or screen-printing [3]. Mask-less printing is the more direct way because no templates are needed and all the layers can be processed seamlessly. Limitation lies in the formulation of suitable inks which can be processed through a printer-head via jet printing. The mask-based printing requires a frame which channels the ink into a specific pattern. In both cases the applied inks need to be sintered and cured. The sintering can be done via thermal, laser or electrical procedures [3]. The curing takes place usually under UV-light.

All of the discussed variables and techniques are relevant in the industrial manufacturing of printed electronic devices. For the hands-on-experiment the screen-printing method was identified as the most feasible technique, which is why this article will focus on screen-printing.

The screen-printing technique is very flexible and versatile compared to the other methods as the substrate can have any surface and the layer-thickness is variable [5]. Thicker layers can increase the stability of the device [4] which was an important factor while developing the hands-on-experiment.

Starting point of the hands-on experiment was a collaboration with the University of Applied Sciences in Munich, where the machine-based screen-printing of a flexible EL-device was demonstrated. The following paragraph summarizes the fabrication process.

1) In the first step a silver-layer is applied on a common A4-overhead transparency (PET), which forms the substrate of the device. The silver-layer builds the base electrode of the device and needs to be sintered in the oven for approx. 10 min (T ≈ 65°C).
2) The second layer consists of an insulating varnish, which works as a dielectric. This layer needs to be cured for approx. 1 min under UV-light.
3) The third layer consists of the semiconductor ZnS:Cu (copper-doped zinc sulfide), which works as a luminophore. It is suspended in an organic solvent and needs to be UV-cured after printing and oven-dried (T ≈ 65°C) for approx. 10 min.
4) The fourth layer consists of PEDOT:PSS, which is a commercially available conductive polymer. It forms the top electrode of the device and allows the light to escape, as it shows transparency. PEDOT:PSS is dissolved in water and needs to be oven-dried (T ≈ 65°C) after application for approx. 20 min.

To print each layer, the substrate needs to be placed into a sieve (a very thin net) and transferred manually into a box, where the printing takes place (Figure 2, left). To apply all the layers precisely on top of each other, markers need to be printed on the substrate beforehand. A computer calibrates the system by optical detection of the markers (Figure 2, right). Then the printing process can start. The ink is resided in front of the substrate and scattered by a rubber blade over the whole sheet (Figure 3, left). The motive can be printed due to the interstitials of the meshes in the net. Then the excess ink is removed by pulling the blade backwards, leaving the ink only in the holes of the sieve. The rubber blade moves only once in each direction as it works with a lot of pressure. For the curing, the substrate is transferred into a UV-chamber (Figure 3, right). To avoid early curing, the room lightning uses bulbs with a reduced amount of blue-light. The machine-based manufacturing process takes around two hours in total.

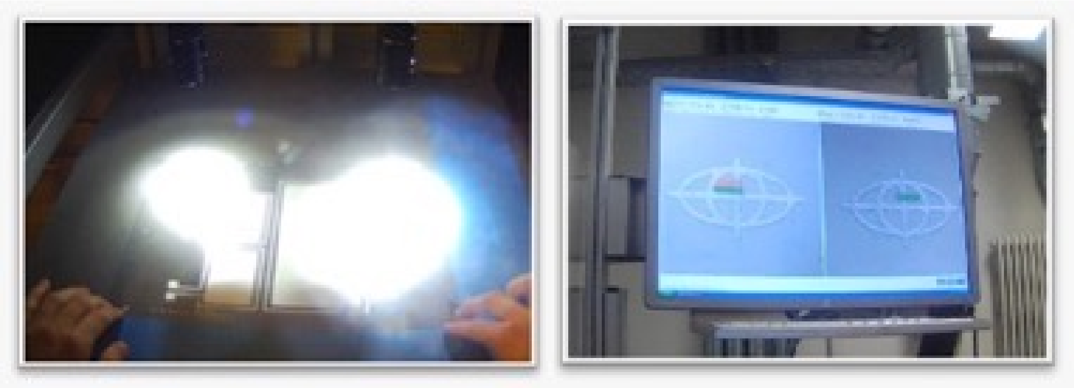

Figure 2. Placing the substrate and sieve into the printing-machine (left) and optical detection of the markers for calibration (right)

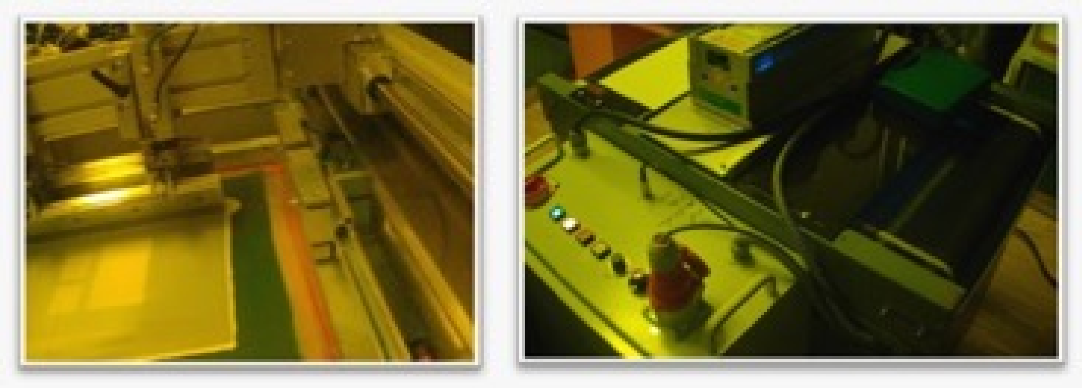

Figure 3. Screen-printer with rubber blade during printing process (left) and professional UV-chamber for curing (right)

3. Didactical Transformation

Table 1. Didactical transformation of the machine-based screen-printing process

Aspect	Didactical adjustments
Low-cost	• A 3x3 cm ITO-foil (indium tin oxide) is used as a substrate, which keeps the size of the device to a minimum and reduces the necessary amounts of the inks. • As the ITO is conductive, it forms the base electrode and the application of a silver-layer can be skipped. • All printing steps are done with a small plastic blade or a spatula instead of a screen-printer. • For the curing a common UV-device for manicure is used instead of a UV-chamber. • For drying and sintering a hairdryer and a common hot-plate are used instead of an oven. • The dielectric has been exchanged by a common insulating varnish from the hardware-store.
Low-risk	• None of the materials are classified as hazardous and the amounts of the chemicals have been reduced to a minimum. Nevertheless, the insulating varnish and the luminophore contain organic solvents which have an odor. • Hence, wearing gloves and working under a fume-hood is recommended.
Low-time	• The machine-based screen-printing of an EL-device takes at least two hours. Since the waiting times for drying, curing and sintering could be reduced to a minimum, the hands-on EL-device can be constructed within 45 min. • It is possible to implement the experiment into a lab-session of 90 min.
Low-tech	• The hands-on EL-device does not need any sophisticated or complex equipment. • Instead of a sieve, two strips of sellotape are used to hold the substrate in place and to define the frame for the printing pattern. • The doctor-blade technique needs a little practice, but is easy to learn and can be applied by learners efficiently. • To supply the device with AC-power, a cost-efficient inverter is used, which works with two AA batteries.

We made several simplifications and adjustments to didactically transform the machine based screen-printing process into a hands-on screen-printing method for teaching purposes. The didactical transformation has been made along the four aspects “low-cost”, “low-risk”, “low-time” and “low-tech” (Table 1) [6].

The following paragraph describes the experiment for building a hand-printed EL-device. By scanning the QR code (or using the link below) you can access a PREZI-learning environment with videos of the experiment (only available in German):

https://prezi.com/view/eAjvmruP9cPQKgTTR0bS/.

3.1. Experiment: Construction of a Flexible Hand-printed EL-device

Materials:

UV-device (Aldi, Quigg, 48W), plastic blade, sellotape, hot-plate, hair-dryer, spatula, AC-inverter (Reichelt Elektronik, EL-inverter Bat), connection cable with crocodile clips, paper sheet (to protect your work space and absorb excess ink).

Chemicals:

ITO-foil (3x3 cm, Aldrich, MFCD00171662), spray can with dielectric (Kontakt Chemie Plastik 70), luminophore (Elantas, Bectron EL 7002 AC), PEDOT:PSS ink (Aldrich, MFCD07371079), conductive silver paint (Conrad, EAN: 4016138097429)

Security advices:

- Wear gloves, safety goggles and a lab coat.
- Work under a fume hood.
- Caution when working with high voltages.

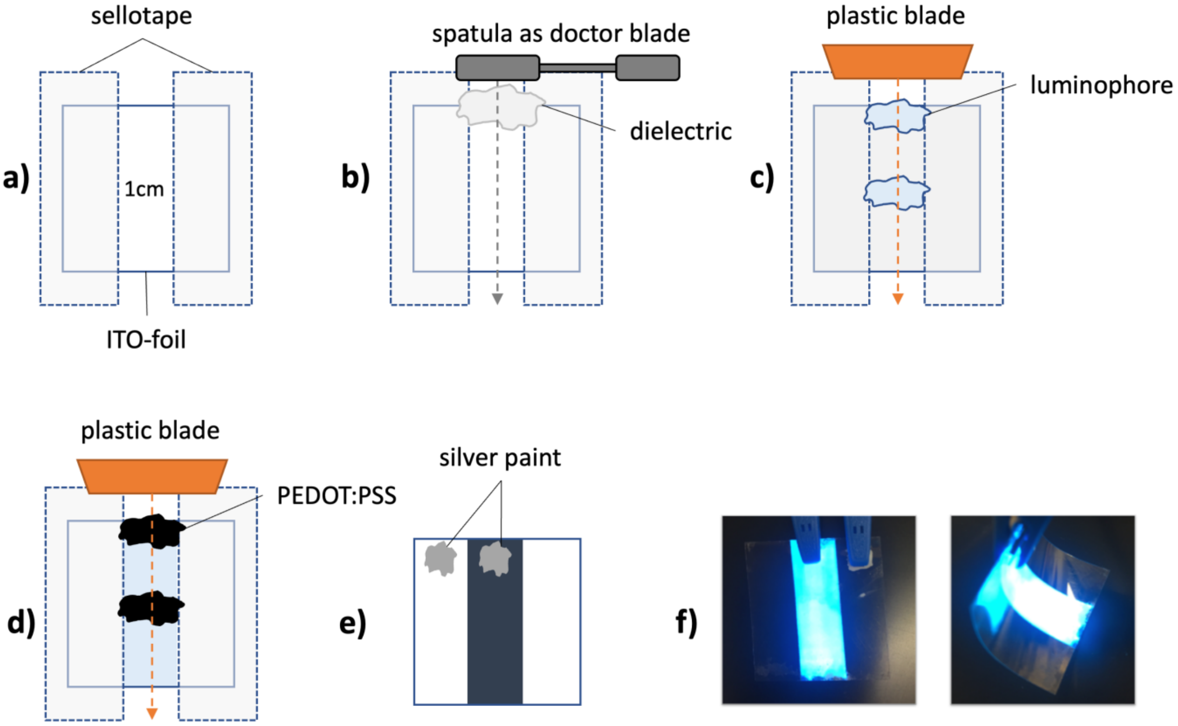

Figure 4. Fabrication steps for the hand-printed EL-device

Experimental procedure:

a) Remove the protection film from the ITO-foil and place it on a paper sheet with the conductive side facing up. Fix the ITO-foil with two strips of sellotape to the paper sheet leaving a gap in the middle of approx. 1cm width (Figure 4a). Note: The exposed part of the ITO-foil defines the luminescent area of the device.

b) Apply a small amount of the dielectric from the spray can to the upper part of the prepared foil. Use the spatula as a doctor-blade and move it downwards with a little pressure and repeat the movement several times until the dielectric is evenly spread over the masked area (Figure 4b). Let it dry for at least 3 min. Note: The plastic blade is not suitable for applying the dielectric.

c) Take a small amount of the luminophore using a spatula and place it on the upper and middle part of the foil as shown in Figure 4c. Repeat the doctor-blade technique using the plastic blade until the luminophore is evenly spread over the masked area. Remove the foil from the paper without untacking the sellotape from the ITO-foil. Place the foil under UV light for 6 min. Remove the foil from the UV-device and put it on the hot-plate for at least 10 min. (T = 65°C).

d) Transfer the foil from the hot-plate to a fresh paper sheet. Place small amounts of PEDOT:PSS ink with the spatula on the foil as shown in Figure 4d. Repeat the doctor-blade technique with the plastic blade until the PEDOT:PSS is evenly spread over the masked area. Dry the layer with a hair-dryer for 5 min.

e) Remove the sellotape completely from the ITO-foil. Apply two small contacts with the conductive silver paint, one on the ITO-foil itself and one on the PEDOT:PSS layer (Figure 4e). Let the silver-paint dry for at least 3min. Your EL-device is ready.

f) Connect the AC-inverter to both of the silver-contacts of your EL-device using the crocodile connection cables. Taking care of the poles is not necessary, as AC voltage is applied. When turning on the inverter, one can observe a bright blue luminescence from both sides of the EL-device, even when it is bent (Figure 4f).

CAUTION: The inverter works with 100 V AC! Do not touch the electrodes while the device is active! People with a pacemaker must keep a safety distance to the inverter!!!

4. Scientific Background

The electroluminescence in a thin-film EL-device is different from that in organic LEDs. While in OLEDs charges are injected from the electrodes into the semiconductor at relatively low DC-voltages [7,8] the EL-device needs 100 V AC to operate.

There are several models explaining the electroluminescence in an EL-device and the scientific debate is still going on, as the fundamental processes are not yet fully understood. One of the most cited models is the *theory of bipolar injection*, which was first published by Fischer in 1962 [9] and modified and optimized by other groups since then. The theory of bipolar injection explains the electroluminescence in powdery polycrystalline copper activated zinc sulfide, which is used in the hands-on device as the luminophore. This model has been adopted and didactically transformed to make the complex theory accessible for undergraduate students.

4.1. The Theory of Bipolar Injection (Simplified for Teaching)

To better understand the fundamental processes leading to electroluminescence simplified energy-band-models are being used (Figure 5).

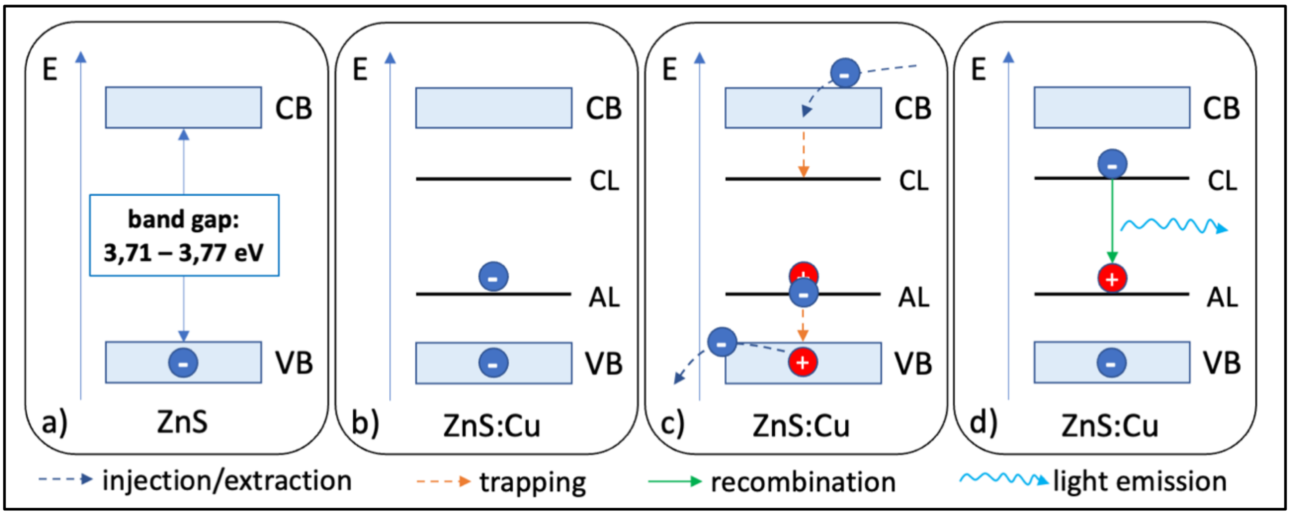

Figure 5. a) Band model of ZnS. In the ground state electrons are located in the valance-band (VB), whereas the conduction-band (CB) is empty. b) Band model of copper doped zinc sulfide (ZnS:Cu) with activator-level (AL) and coactivator-level (CL). In the ground-state electrons are located in the VB and AL, whereas the CB and CL are empty. c) During electroluminescence electrons are injected into the CB and get trapped in the CL. Simultaneously, the electrons from the VB are extracted, leaving a hole (i.e. a positive charge) behind. These holes get trapped in the AL. d) When trapped electrons on the CL encounter trapped holes on the AL, the charge carriers recombine under emission of visible light

The semiconductor-layer mainly consists of copper-doped zinc sulfide (ZnS:Cu). ZnS itself is a UV emitter with a bandgap of around 3,71 - 3,77 eV [10] (Figure 5a). The copper-doping introduces two new energy levels in the band structure of the semiconductor, termed as activator-level (AL) and coactivator-level (CL) (Figure 5b). The CL lies slightly below the conduction-band (CB) and acts as traps for electrons injected in the CB (Figure 5c). The AL lies slightly above the valance-band (VB) and both energy levels are occupied with electrons in the ground state (Figure 5b). When an electron is extracted from the VB, a hole is left behind. A hole can be considered as an unoccupied low-energy state in an electronic system, which attracts electrons with higher energy. Consequently, the electron from the AL transfers to the vacancy in the VB, which indirectly transfers the hole from the VB to the AL, where it is trapped (Figure 5c). Technically, the extraction of an electron equals to the injection of a hole.

When trapped electrons on the coactivator-level encounter trapped holes on the activator-level, the charge carriers recombine under emission of visible light (Figure 5d) [11].

To understand how electrons and holes are injected into the ZnS:Cu layer, it is necessary to consider the luminophore in detail. For a vivid visualization, a simplified structure-model is being used, which is derived from a horizontal cutout of the flipped device as shown in Figure 6. The semiconductor layer does not only consist of copper-doped zinc sulfide, but also contains small crystallites made from copper-I-sulfide (Cu_2S), which are embedded in the polycrystalline structure of the semiconductor [12] (Figure 6).

These Cu_2S-crystallites are needle-shaped and have a band-structure similar to a conductor with a narrow band gap of approx. 1,2 - 1,7 eV (Figure 6, upper right corner) [13].

All processes shown in Figure 7 occur around a vast number of such crystallites. For simplification the models in Figure 7 consider only one Cu_2S-crystallite.

When an electric field of around 100 V (AC) is applied to the EL-device, the following processes can be assumed.

1. Due to the relatively high conductivity of the Cu_2S-crystallites the electric field concentrates on both ends of the needle-shaped crystallites (Figure 7a) [12]. The high voltage forces the injection of charge carriers from the Cu_2S-needles into the semiconductor-layer on both ends, which can be considered as a bipolar injection mechanism. The injected electrons move towards the positive electrode, while the injected holes move towards the negative electrode. On their way to the electrodes, the charge carriers get trapped in the activator- and coactivator-levels of the semiconductor as discussed before (Figure 7b & Figure 5c) [14].
2. In the next phase of the alternating current the electric field converts and consequently the direction of the bipolar injection of electrons and holes inverts as well (Figure 7c). The injected charge carriers start to move towards the electrodes and encounter the trapped carriers with opposite charge from the previous phase [15]. This encounter leads to the formation of electron-hole-pairs (i.e. excited states), which recombine under emission of blue-light (Figure 7d & Figure 5d).

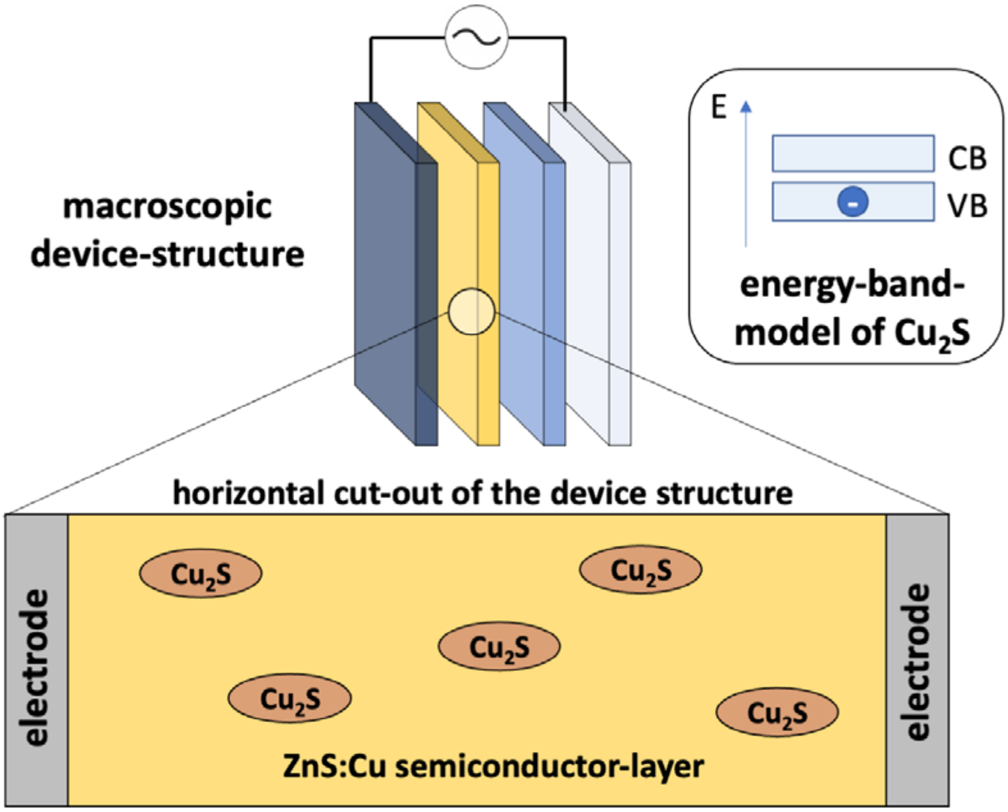

Figure 6. Structure-model derived from the flipped device. The insulating varnish is neglected in the structure-model for simplification. The Cu_2S-crystallites (brown ellipses) have a narrow band-gap (see band-model in the upper right corner) and play a vital role for the bipolar injection mechanism

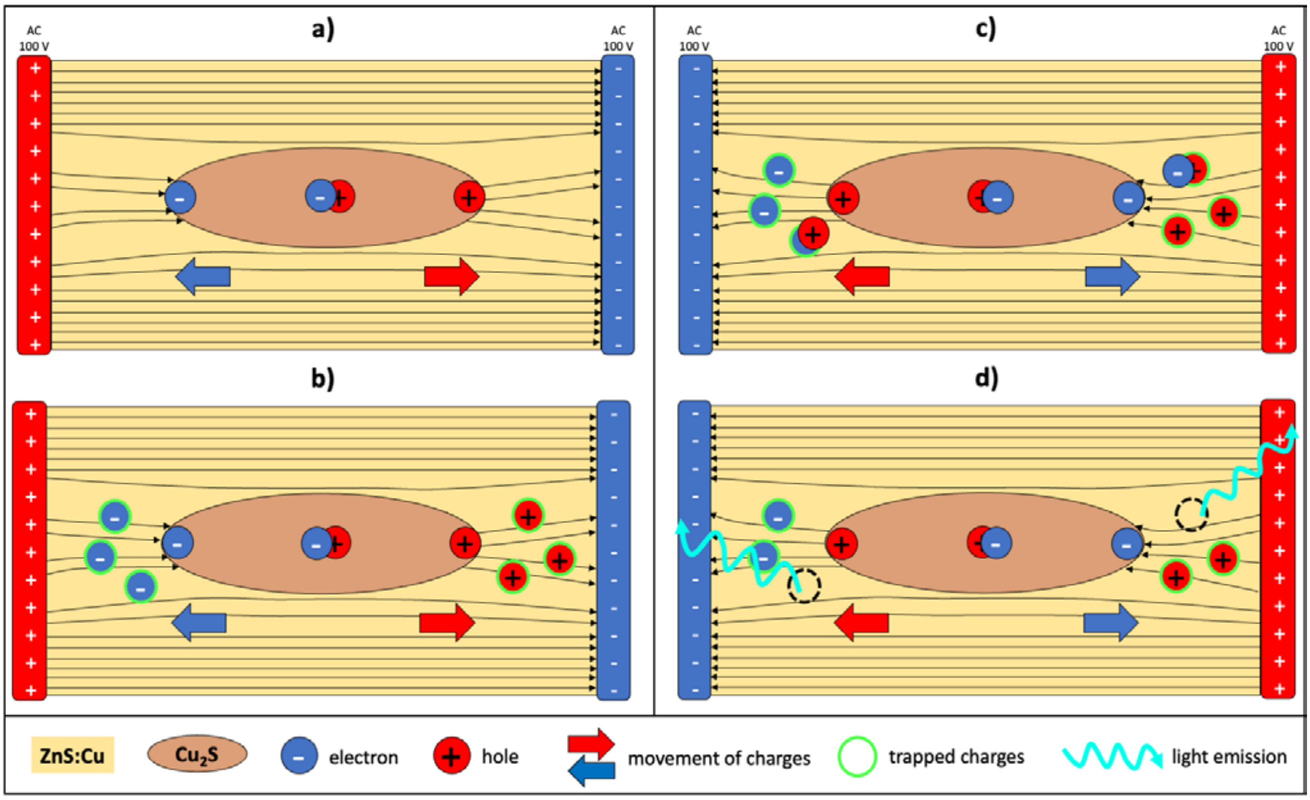

Figure 7. a) Charge carriers are released from Cu_2S-crystallites into the semiconductor layer due to the high electric field. b) Charge carriers move towards the electrodes and get captured in the traps of the semiconductor. c) Phase change of alternating current inverts the direction of the bipolar injection. The injected charge carriers encounter trapped ones with opposite charge. d) Trapped electrons and holes recombine under light emission

5. Discussion

Regarding the hand-printed EL-device, we would like to point out, that the doctor-blade technique indeed imitates a printing process. This needs to be emphasized, as people usually are not familiar with the screen-printing and therefore don't relate the scattering of ink with a blade to a printing-technique.

Regarding the theory, we must emphasize that our *simplified theory of bipolar injection* neglects several aspects of Fischer's original theory and focuses only on selected fundamental processes, which we identified as most relevant to explain the electroluminescence in the EL-device for undergraduate students. For instance, our model does not explain the function of the dielectric, which is (among others) to prevent current-flow from the electrodes into the semiconductor layer.

We are still working on the teaching materials and our models can be considered as "under construction" and we would like to share them for discussion.

6. Conclusion & Outlook

The implementation of cutting-edge research topics into science teaching is a promising way to motivate learners for STEM. The development of "school-tailored" experiments is a key element for a successful implementation.

The aim of this work was to transform the process of the machine-based screen-printing of electronics into a hands-on experiment, which allows students to experience and understand this innovative technology. The presented hands-on experiment does not need any expensive or sophisticated equipment (approx. 2€/device) and can be done within 45 minutes, which makes it suitable for school-lessons.

Furthermore, we could develop a simplified model to explain the complex theory of electroluminescence via bipolar injection. The next step of our research-cycle is to evaluate the experiments and teaching materials along with students and teachers in our academic school-lab and in schools. Furthermore, we are working on a hand-printed 7-segment EL-display to interconnect this innovative topic with physics and informatics for an interdisciplinary approach.

Additionally, we are developing a teaching kit, which will contain all necessary materials for building hand-printed EL-devices with students in a lab-session.

Besides the chemicals and technical components, the teaching kit will also contain a booklet with instruction manuals, hazard-assessments, work-sheets and more. Also, multimedia teaching tools will be provided on our website. Our aim is to enable teachers to implement this innovative topic in their classes "out of the box". The teaching kit will be available for order (in the EU) on the following website soon (use the link or scan the QR code).

https://boxperiment.de/printed-electronics.

Acknowledgements

We thank Dr. Wolfgang Schmidt for demonstrating the mechanical screen-printing of an EL-device in his institute in Munich.

We thank Dustin Freimuth for helping us to develop learning-models for the theory of bipolar injection.

We thank the Deutsche Forschungsgemeinschaft (DFG) (GRK 2482) for financial support.

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