Printed Organic Diodes and their Integration for Rectification and Energy Harvesting

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Outline

- *TUT Introduction*
  - Town and university
  - Organic and printed electronics
- Gravure printed thin film diodes
  - Materials and architecture
  - Interfaces and effect on device performance
- Rectifier Circuits
  - Half-wave vs. full wave
  - Printed organic charge pump circuits
- Printed RF energy harvesters
  - AUTOVOLT project
  - Printed RF harvester and integration to capacitor

Tampere: “Manchester of the North”

- Founded as a market town in 1775, now third largest city in Finland (213,000 inhabitants)
- Major growth during industrial revolution (thanks partly to Tammerkoski rapids)
- Situated between 2 large lakes, Näsijärvi and Pyhäjärvi
- Industry includes paper, mining machinery, glass manufacturing equipment – and mobile phones!

Tampere University of Technology (TUT)

- Established in 1965
- Started operating in the form of a foundation in 2010
- 11,600 students (2009)
- Strong tradition of university/industry cooperation

Printed Electronics at TUT

Professor Donald Lupo

Organic Electronics Group

Head of group: Prof. Donald Lupo
Senior scientist: Dr. Sampo Tuukkanen

- electronic ***devices*** utilizing solution processable materials and printing processes
- diodes, transistors, sensors, supercapacitors

Printable Electronics Group

Head of group: Dr. Matti Mäntysalo

- electronic system ***integration*** and manufacturing concepts utilizing printing processes
- interconnections, systems, reliability and performance analysis

Over 250 m^2 dedicated lab space, incl. dust-free processing laboratory of 60 m^2 (non certified but close to ISO 14644-1 class 5)

Printing equipments: Ink-jet (2x iTi MDS 2.0, Dimatix DMP-2831), Gravure (NSM Labratester), Flexo (RK Flexiproof 100), Screen (DEK)

Variety of other deposition and processing tools and equipments for characterisation of material properties and electrical performance (spin coater, fibrelaser, drop watcher, semiconductor parameter analyser, profilometer, etc.)

Environmental test equipments (thermal chambers for shock and cycling, vibration, salt tests, drop tests, etc.)

Variety of analysis tools in University (profilometers, SEMS, AFM, etc.)

PRINT LAB

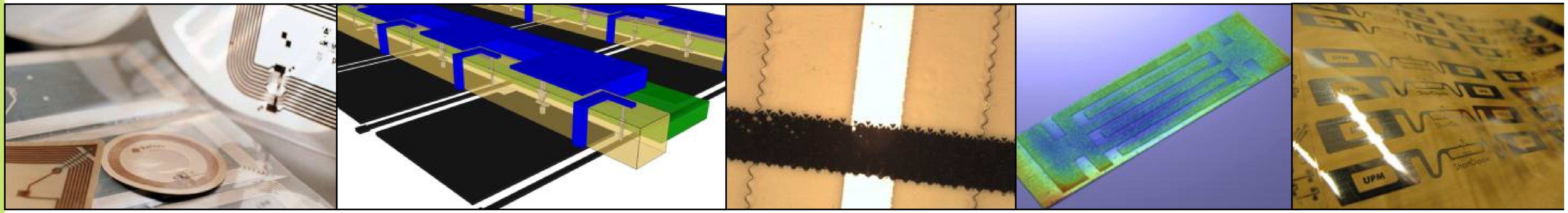
Organic Electronics Group

- ***Focus: understanding how printing affects materials, interfaces and device/system performance***
- Printability of various formulations of electronic materials
- Materials compatibility and interfacial properties
- Fabrication of devices
- Characterisation of printed materials, structures and devices
- Processes: gravure, screen, inkjet

Activity areas

- Printed diodes, transistors and sensors
- Printed energy harvesters
- Printed supercapacitors
- Printed circuits
- Printed photovoltaic modules

- Concept development
  - *innovative and novel combinations of materials, structure and manufacturing*
- Scalable unit processes
  - *lab-scale unit processes that are scalable and feasible to cost-effective industrial production*
- Components and sub-systems
  - *single components (diode, transistor, sensor, etc.) or simple sub-systems (2-3 integrated components + recurring multiples)*

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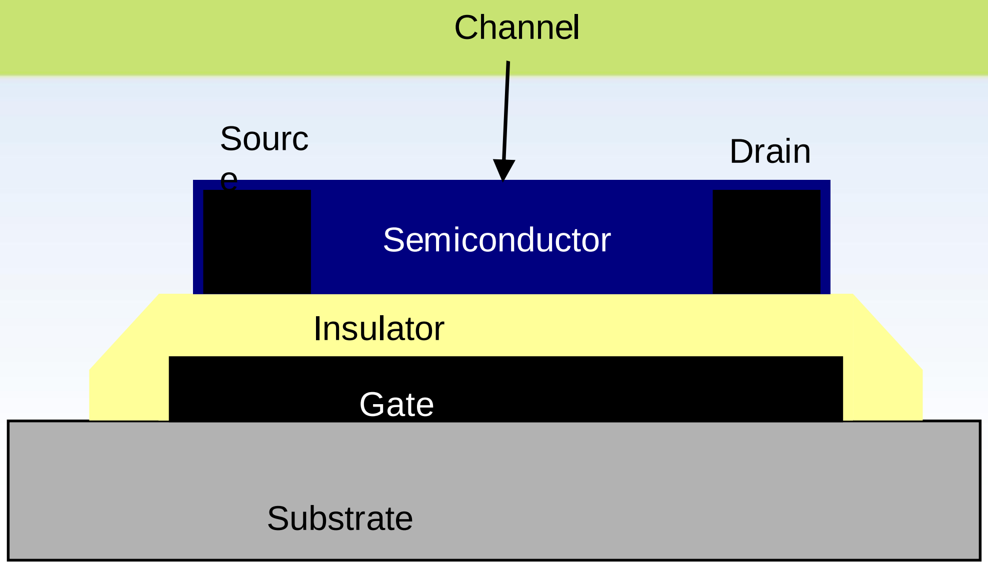
Challenges for printing organic circuits

- Formulation
  - Mass printing needs higher viscosity
  - Traditional printing industry additives won‘t work
- Feature size
  - Printing makes larger structures and these mean lower speed, larger footprint etc
- Registration
  - Limited by both machine and substrate unless digital distortion correction possible
- Trade-off between feature size and throughput

Organic thin film transistors



The conduction in a thin *channel* of semiconductor between two electrodes (*source* and *drain*) can be turned on and off by adjusting the voltage at a *gate* electrode separated from the semiconductor by a thin insulator (*gate dielectric*)

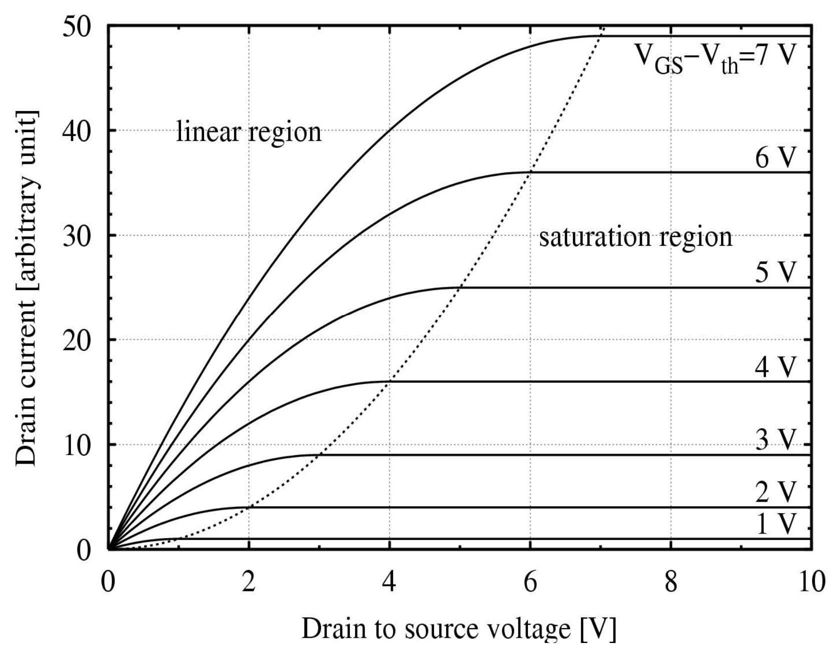
Current flow is *horizontal*

Applications in logic, display backplanes, RFID...

Critical parameters include

- Charge carrier mobility
  - Issue with organic semiconductors
- Channel length
  - Limited by printing resolution
- Gate overlap
  - Limited by registration
- Field strength and uniformity
  - Limited by thickness and uniformity of insulator

Several challenges for printing and organics



Organic thin film diodes

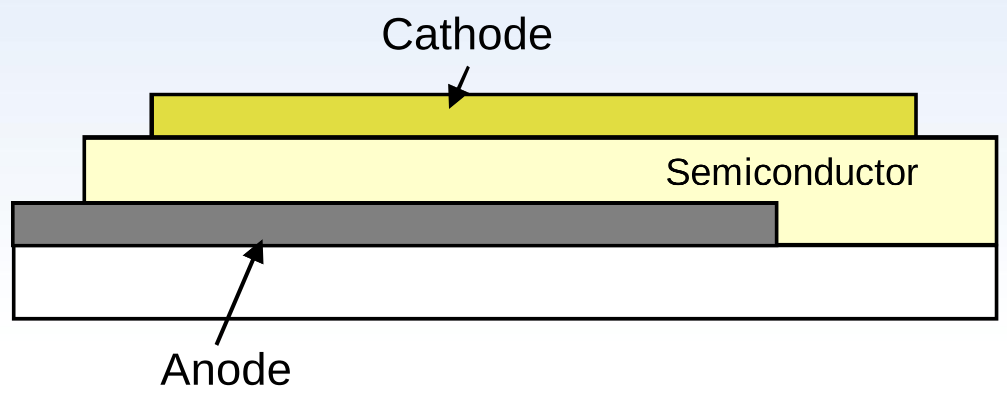
Most organic thin film diodes (TFDs) are Schottky diodes

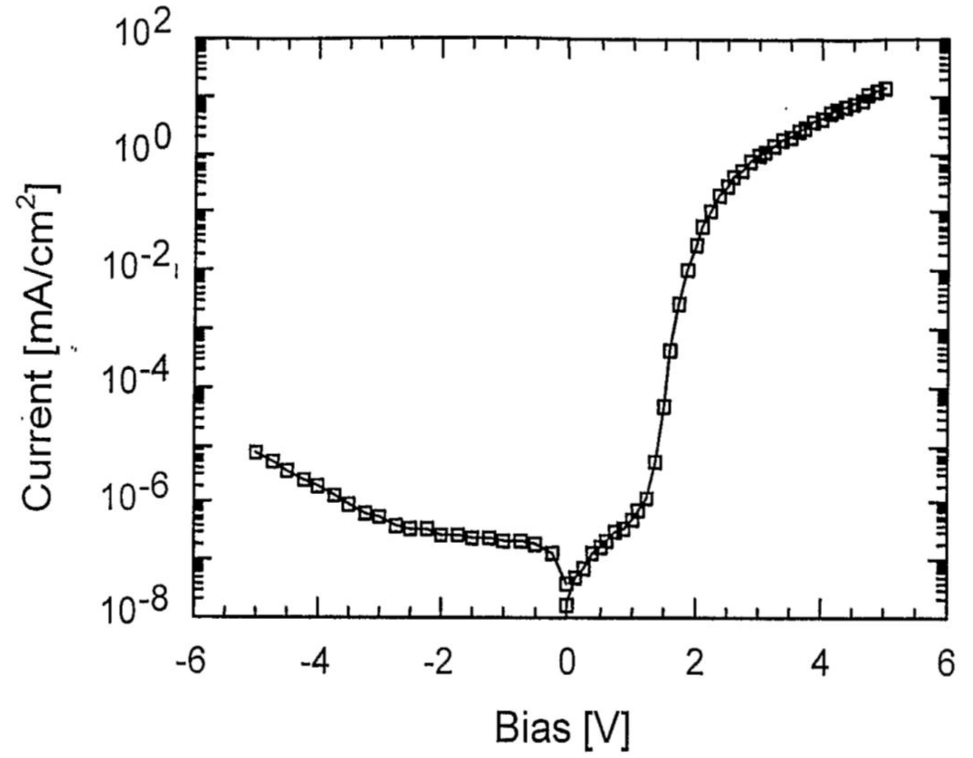
- Metal/semiconductor contacts are Ohmic in one bias and blocking in the other
- In forward bias, charges are injected and current can flow
- In reverse bias, the charge injection barrier is high
- High rectification ratio

Current flow is *vertical*

Lower requirements for charge carrier mobility and resolution/registration than TFTs

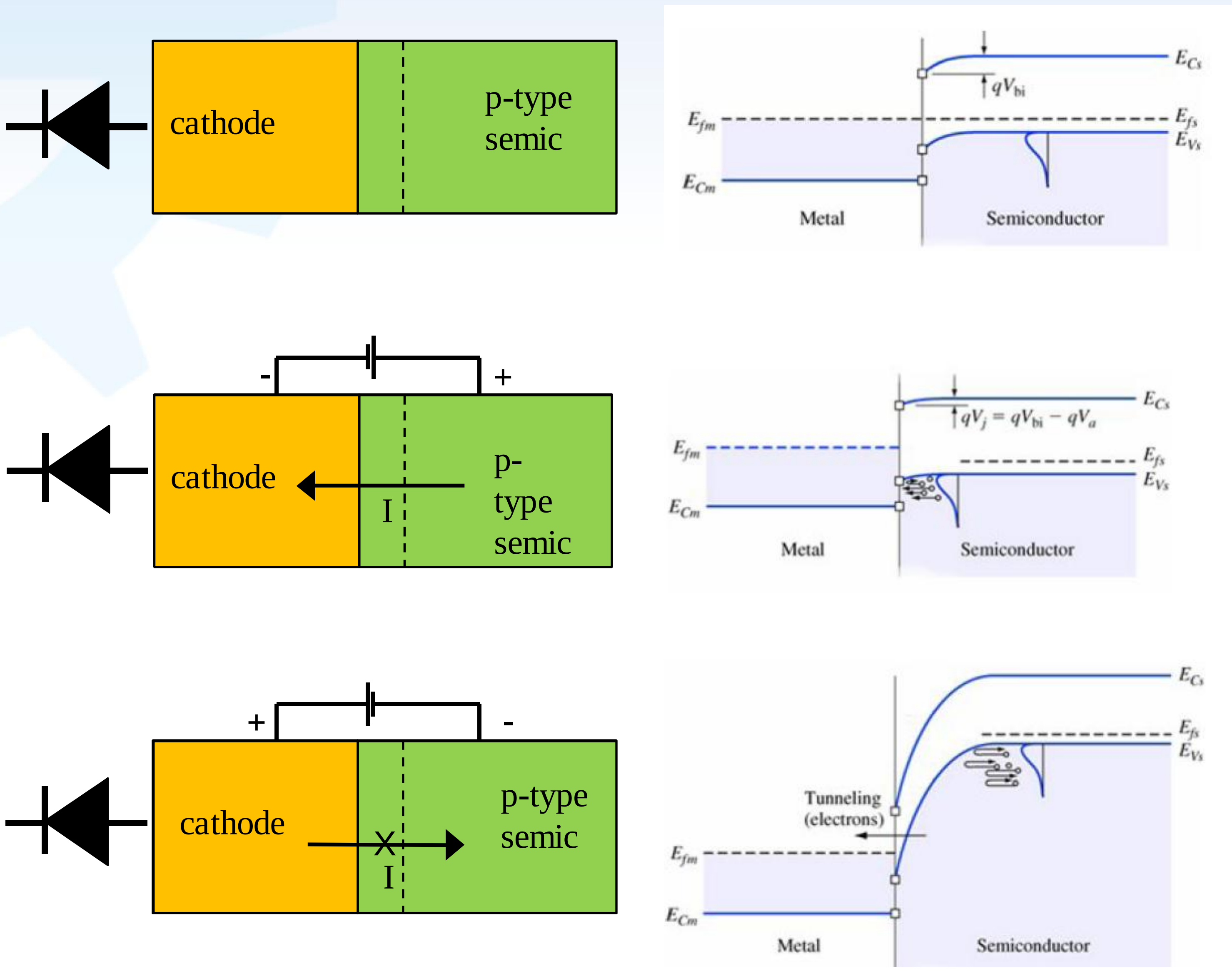
Fewer issues for printing



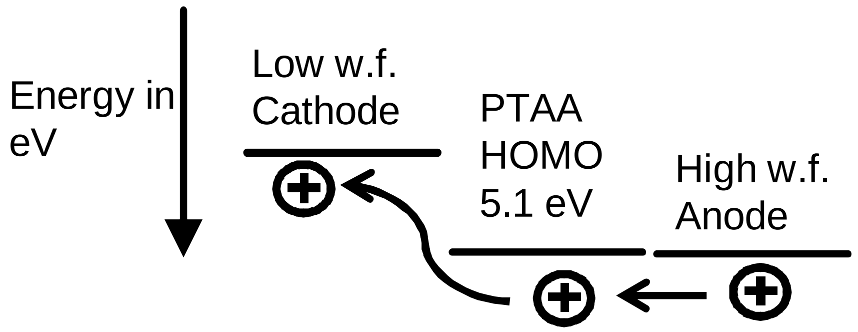


Cebrite, patent application WO04/66410 (2004).

Diode architecture - expectation

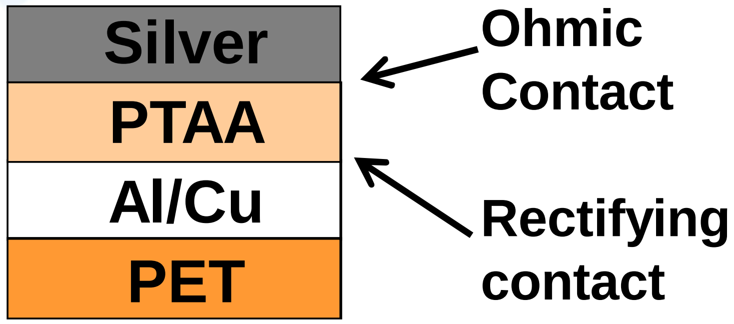


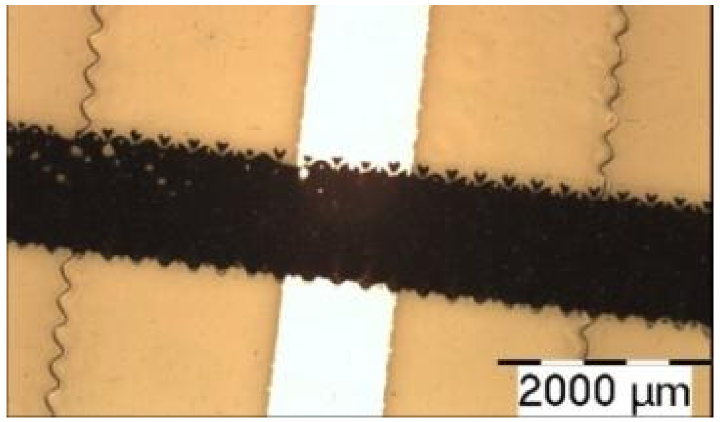
- Organic Schottky diodes
  - P-type semiconductor
- Semiconductor mobility
  - Pentacene 0.15 cm^2 / Vs
  - ***PTAA 0.002 cm^2 / Vs***
- Electrodes
  - PTAA HOMO at 5.1 eV
  - Cathode: calcium, aluminium…
  - Anode: platinum, gold…



Diode fabrication

- Simple three-layer vertical diode structure
- High-throughput printing process manufacturing

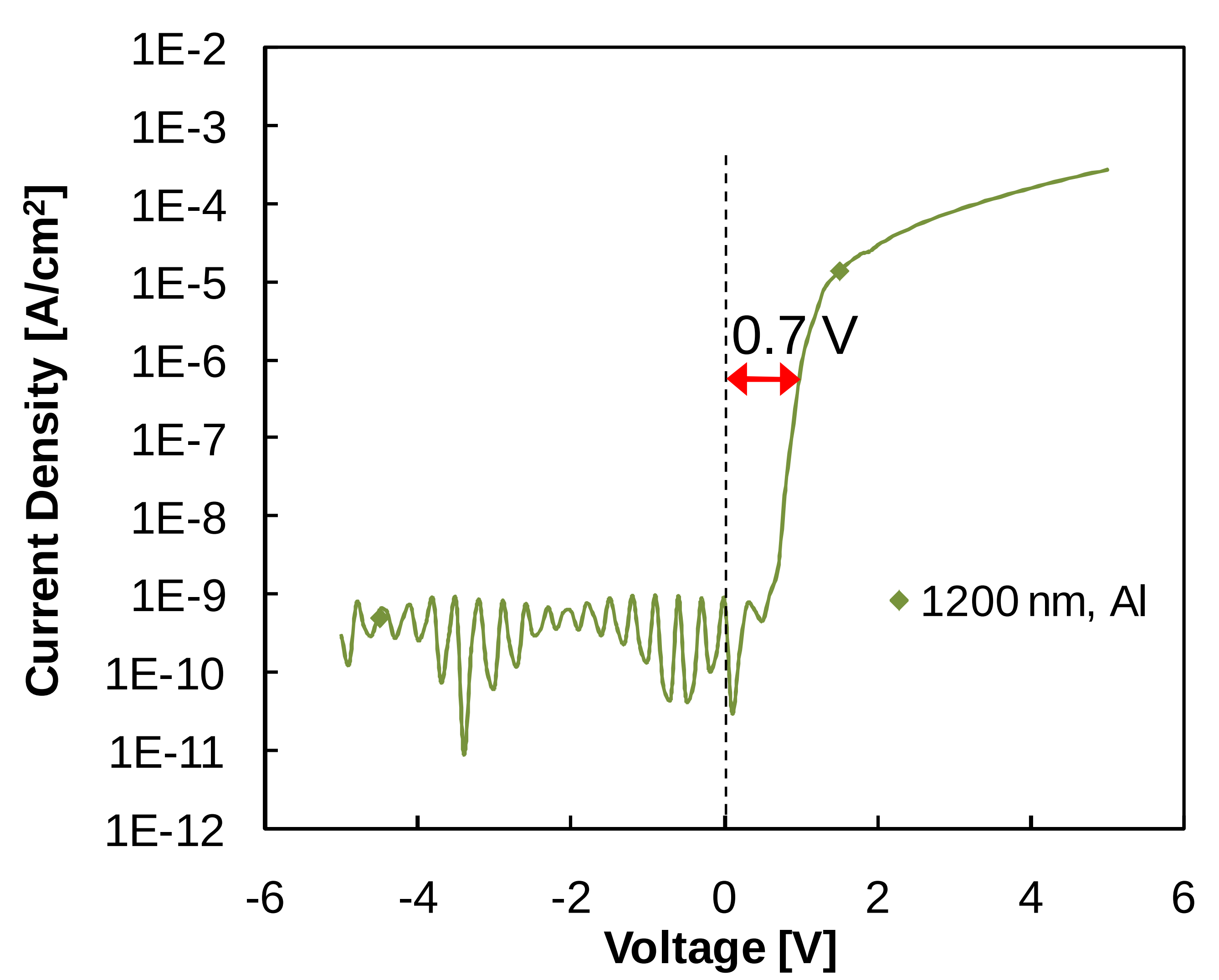




- Wet etched aluminium/copper (screen printed etch resist)
- PTAA and silver gravure printed
- Diodes fabricated and characterised in ambient conditions
- No fine patterning or in-line vacuum processes

Diode Characteristics – Al cathode

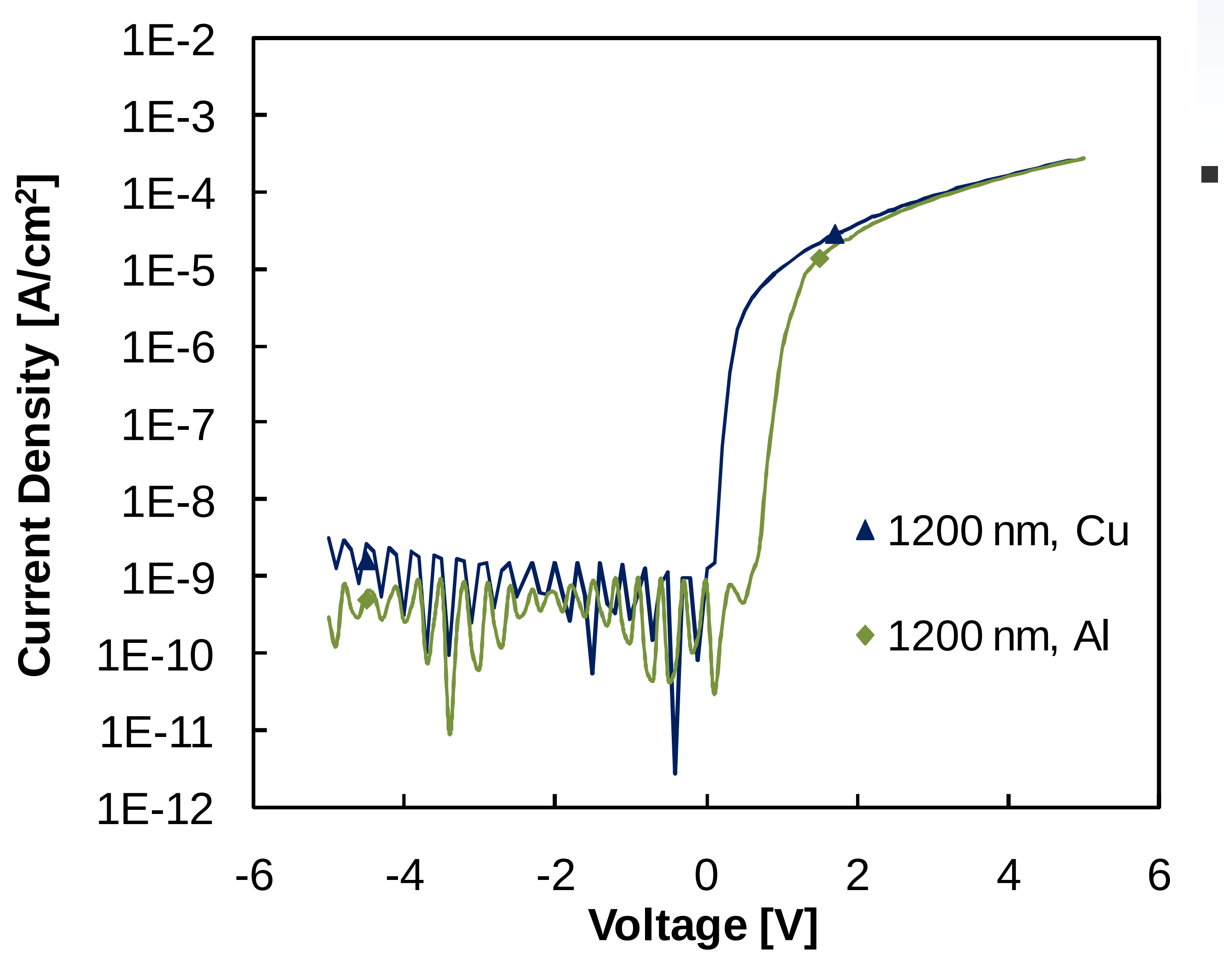
- Aluminium, a current density of 0.1-0.5 mA



- Rectification ratio over 10 000
- Threshold voltage, probably due to oxide layer on Al
- Slow response (see later slides)

Diode Characteristics – Cu cathode

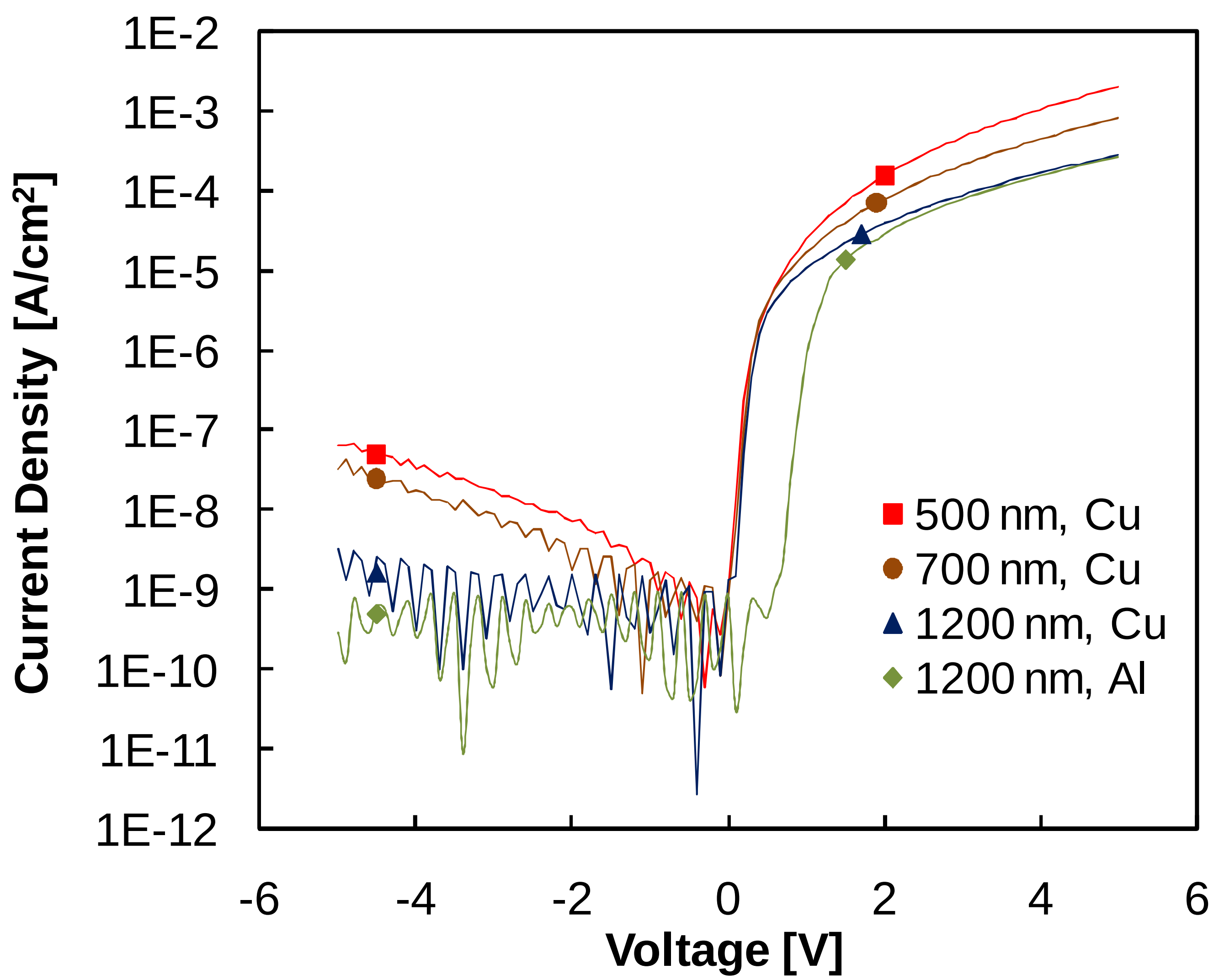
- Copper, a current density of 0.3 mA/cm^2



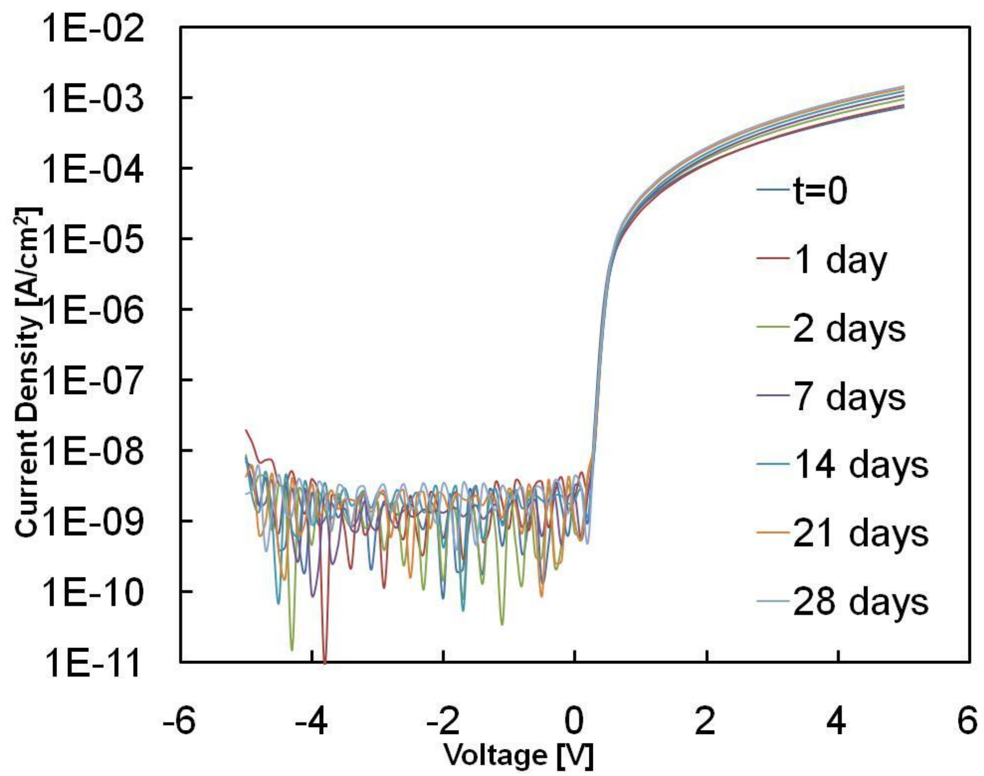
- **Same rectification ratio and forward current as Al but no threshold**

Diode Characteristics

- At 5 V, a current density from 0.3 to 2 mA/cm² for semiconductor thicknesses of 500 to1200 nm



- No significant degradation in four weeks after fabrication

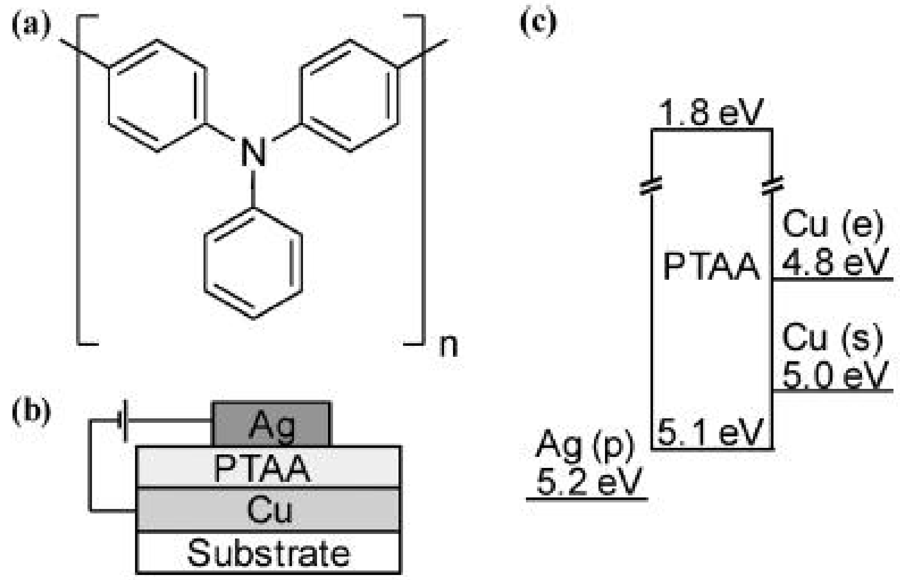


Interfaces in printed organic diodes

- Good results for Cu/PTAA/Ag diodes
- The i-V curve shows clearly that Cu is the cathode and Ag is the anode
- But according to the literature, the work function of Ag is 4.3 – 4.7 and Cu‘s is ca 4.7
- >>> in principle, this shouldn‘t work!
- Plus, the rectification ratio is 100,000 with sputtered Cu and 1000 with evaporated Cu
- So, something else was happening

Interfaces in printed organic diodes – Kelvin probe

- A Kelvin probe (Au reference in air) was used to *estimate* the work functions of the Cu and printed Ag electrodes
- Measured work function of Ag is consistent with oxidation to Ag_2O
- Even accounting for the uncertainty of Kelvin probe measurements, the Cu values do not explain cathode behaviour



K. Lilja et al., ACS Applied Materials and Interfaces **3**, 7 (2011)

Interfaces in printed organic diodes – i-V Curves

- Plot log J vs log V for sputtered and evaporated Cu diodes
- When current is space charge limited, $J = 9\varepsilon_r\varepsilon_0\mu V^2/8L^3$ (Child's law)
- SCLC starts ca 0.2 V for evaporated Cu and ca 2 V for sputtered Cu on PET
- Clearly a difference in the two interfaces!

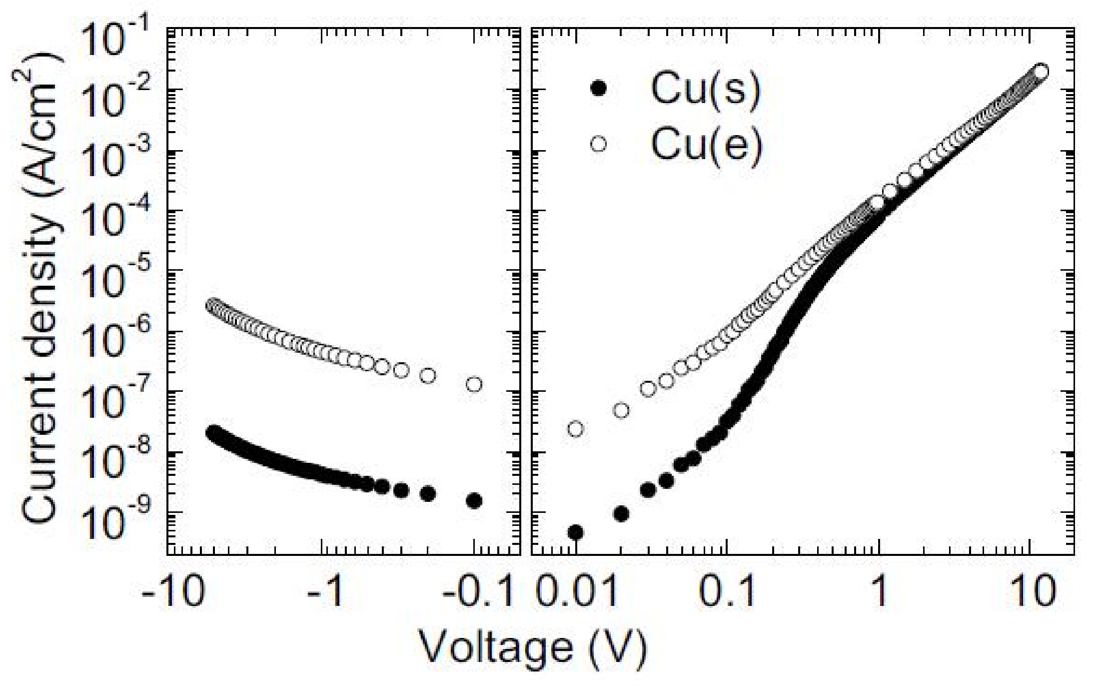
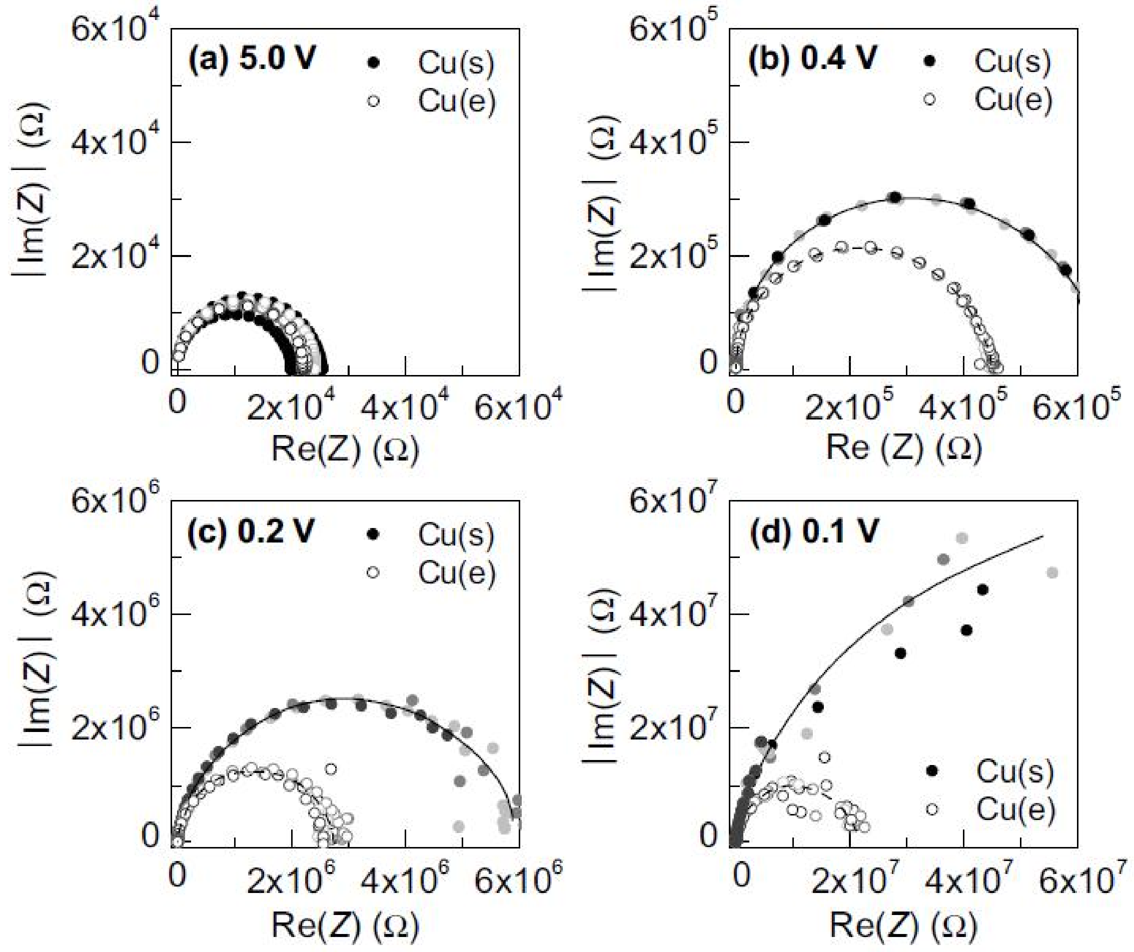


Figure 1. Log *J*–log *V* performance of diodes with sputter-deposited [Cu(s)] and evaporation-deposited [Cu(e)] copper cathodes.

K. Lilja et al, J. Phys. D. **44**, 295301 (2011)

Interfaces in printed organic diodes – impedance spectra

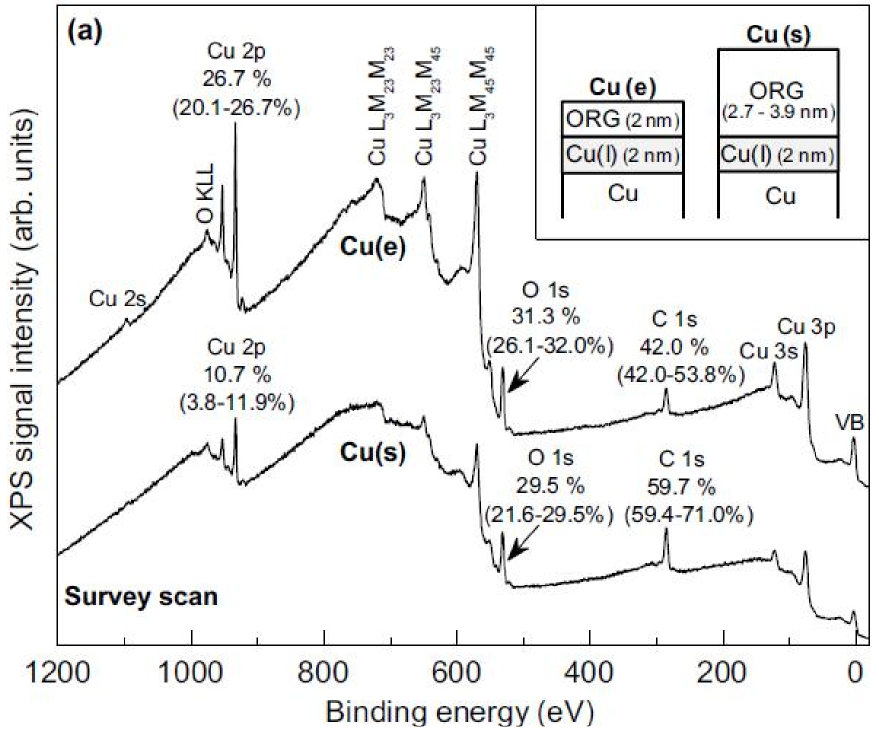
- Impedance spectra measured at different voltages for diodes with sputtered and evaporated copper from 1 MHz – 10 Hz.
- @ high frequency: only geometric capacitance
- @ high bias no difference
- @ low bias difference at low frequency, indicative of interfaces
- >> indicates changes in the metal-semiconductor interface

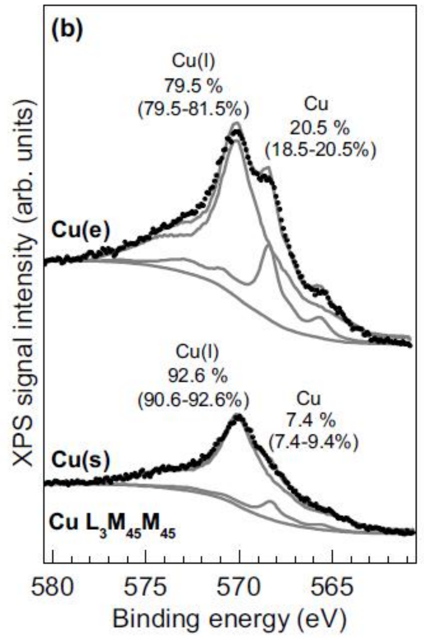


Cole–Cole plots of the diode impedance at forward bias voltages of 5.0 , 0.4, 0.2 and 0.1V. The frequency increases from right to left from 10 Hz to 1 MHz. Source: K. Lilja et al, J. Phys. D. **44**, 295301 (2011)

Interfaces in printed organic diodes – XPS data

- XPS data indicate presence of Cu(I) and organic in both layers but clearly more of each in the sputtered copper
- Cu(I) believed to be Cu_2O
- organic layer could be partially PET but other impurities as well
- Experiments on ALD of PET for controlled reference in progress

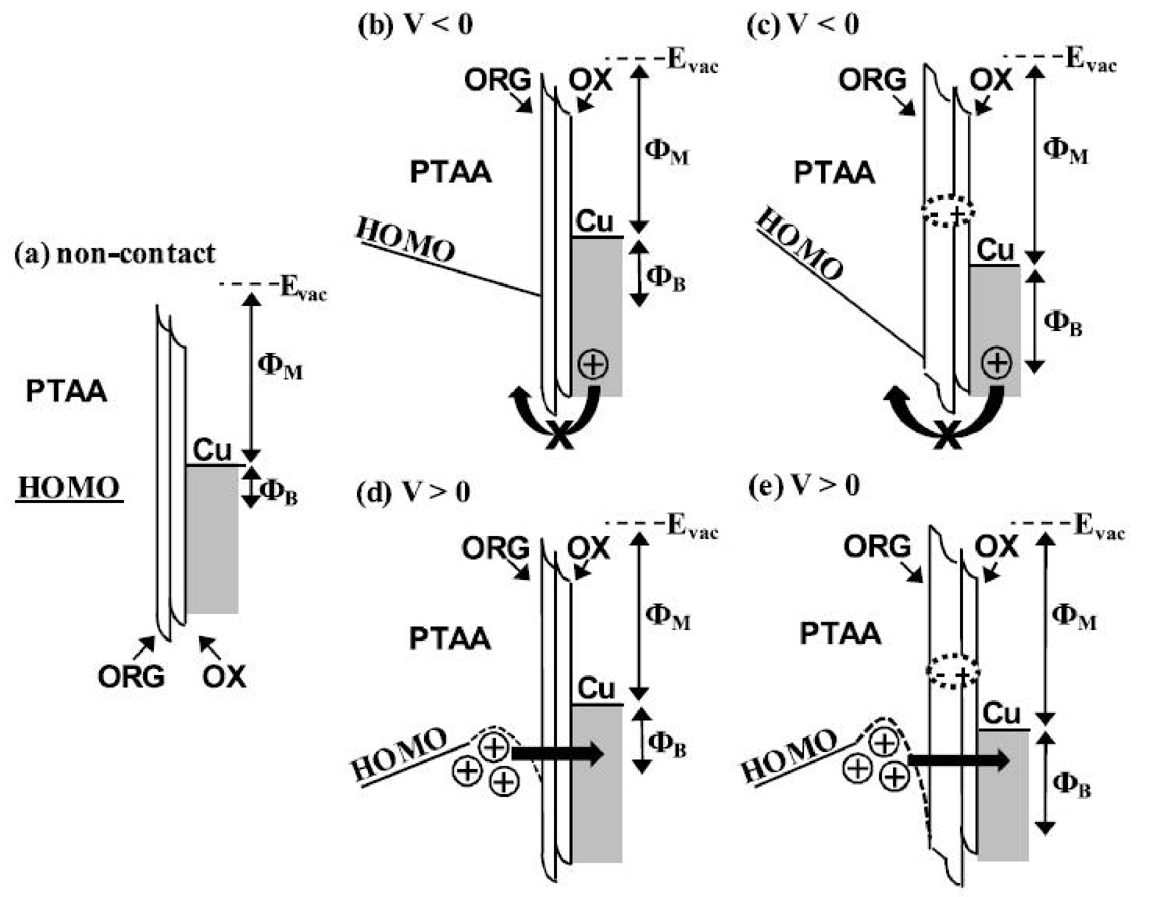




K. Lilja et al, J. Phys. D. **44**, 295301 (2011)

Interfaces in printed organic diodes – interfacial layer

- Based on impedance and XPS data, a model can be proposed
- Effective Schottky barrier is increased beyond measured value when semiconductor and metal (+ Cu_2O and organic) are brought into contact.
  - pinning of Fermi level in organic semiconductor due to tailing of wave function from metal
  - change in pinning due to intermediate dielectric
  - orientation of dipole potential between two interlayers has further effect
- Dual dielectric layer present in both evaporated and sputtered Cu >> can explain the fact that rectification is seen in both cases. Thicker layers in sputtered Cu enhance the effect
- In forward bias, field is high enough to assist tunnelling >> identical forward currents at sufficiently high bias
- Modelling at Åbo Akademi supports the proposed mechanism



Simplified model for the diode Schottky contact. Source: K. Lilja et al, J. Phys. D. **44**, 295301 (2011)

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- Printed RF energy harvesters
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Organic rectifier diodes for RF

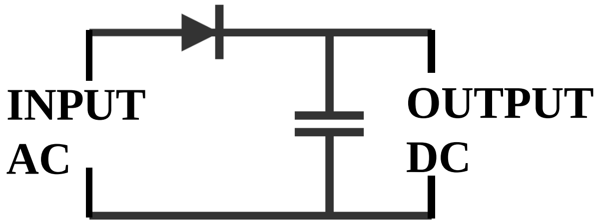
Rectifiers in RFID

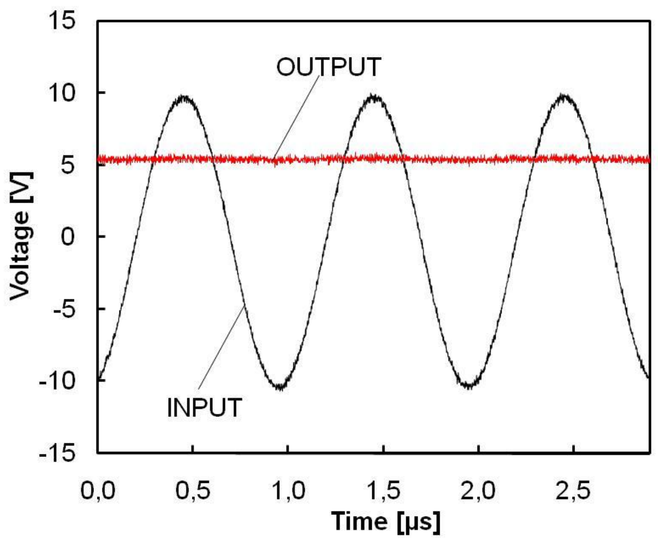
- A rectifier circuit converts the AC signal picked up by the RFID antenna to a DC signal for the chip to use
- 50 MHz rectifiers by Steudel et al. (Nat. Mater. 4 (2005) 279)
- 433 - 869 MHz integrated rectifiers by IMEC (Holst Centre)
  – Based on vacuum processing/shadow masking
- Spin coated P3HTdiodes with the -3dB point at 2 MHz by Kang et al. (Thin Solid Films **518** (2009) 889)

Goal: make an RF rectifier using only mass printing processes

Key issues

- Mobility (response of OSC to AC field)
- Capacitance (size and thickness of diode)





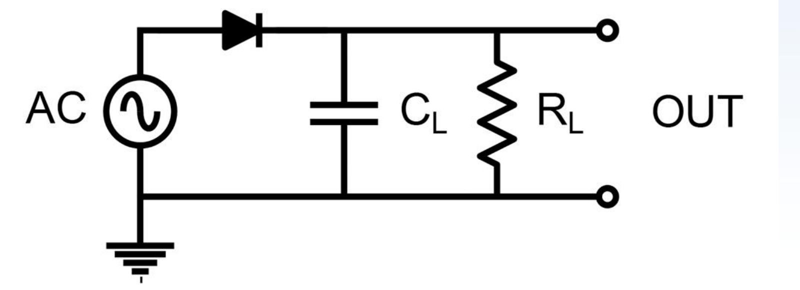
S. Steudel, K. Myny, V. Arkhipov, C. Deibel, S. De Vusser, J. Genoe, P. Heremans, Nat. Mater. 4 (2005) 279.

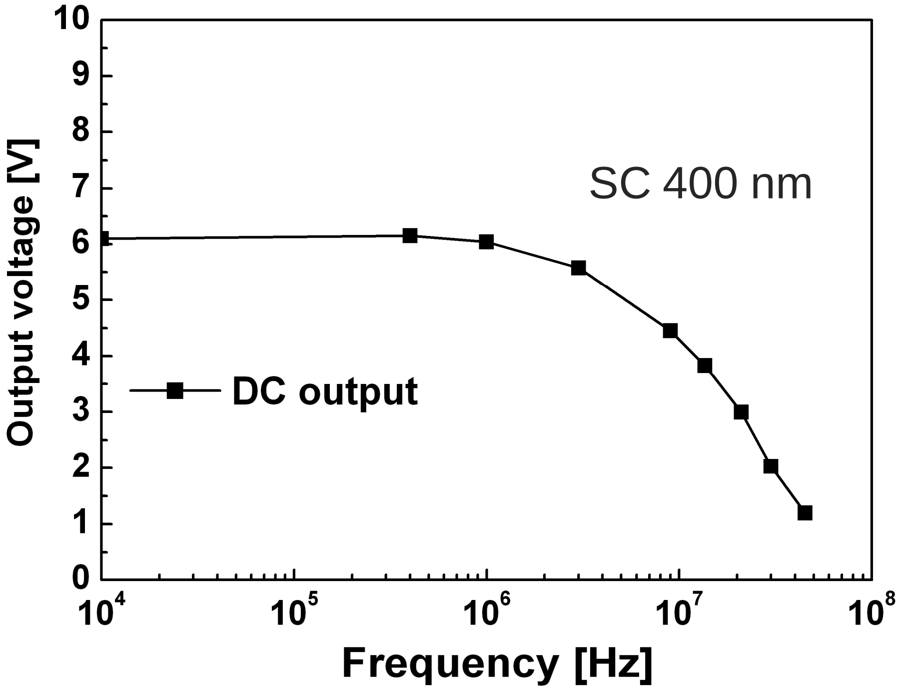
Half-wave rectifier

- Half-wave rectifier circuit
  - Discrete capacitor and resistor
    - C_L ~ nF
    - R_L usually 1 MΩ
  - Also printed capacitors have been used
    - $C_L \approx 0.5 – 2$ nF/cm^2

- Half-wave rectifier output with 10 V AC input
  - 6.1 V at low frequencies
  - 3.8 V at 13.56 MHz

  - Better output with thinner SC layers
    - Lower yield

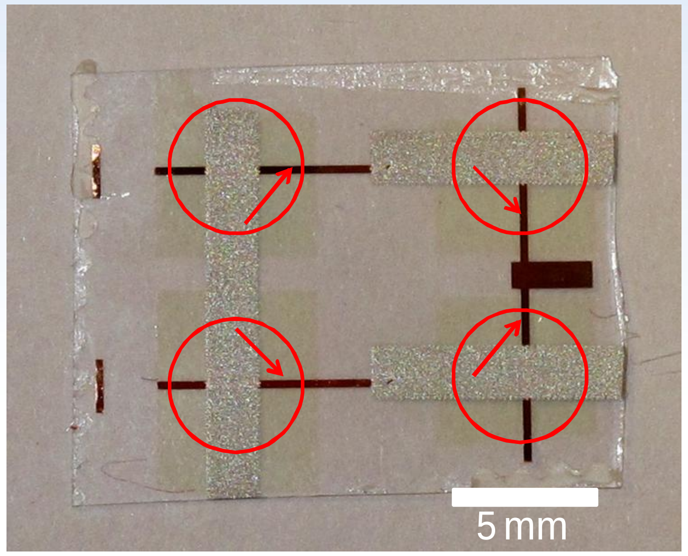


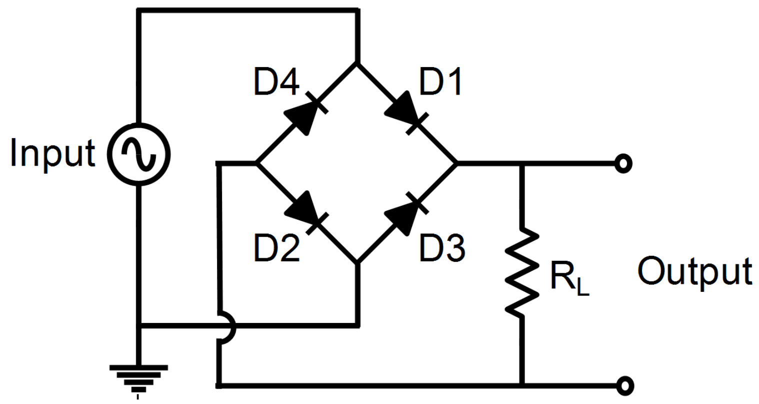


P. Heljo et al., IEEE Trans. Electron. Devices, in press

Full-wave bridge rectifier

- Full-wave rectification for better output characteristics?
- Lower ripple at low frequency application
- Lower output voltage
  - Voltage drops over two diodes
  - Slower device
    - Lower operation frequencies
- Also lower output power





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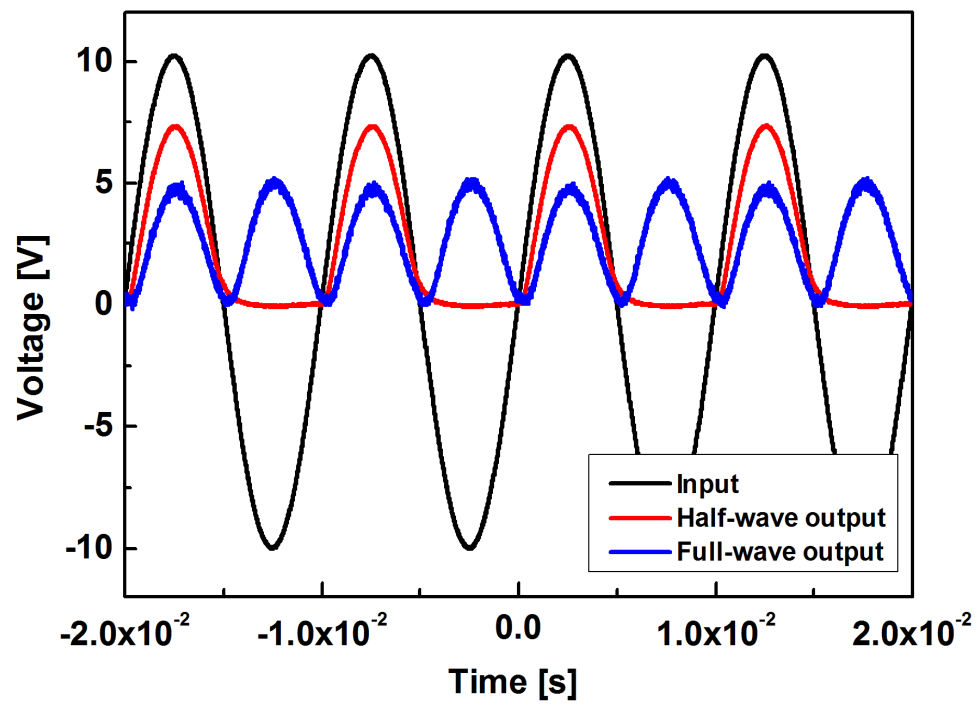
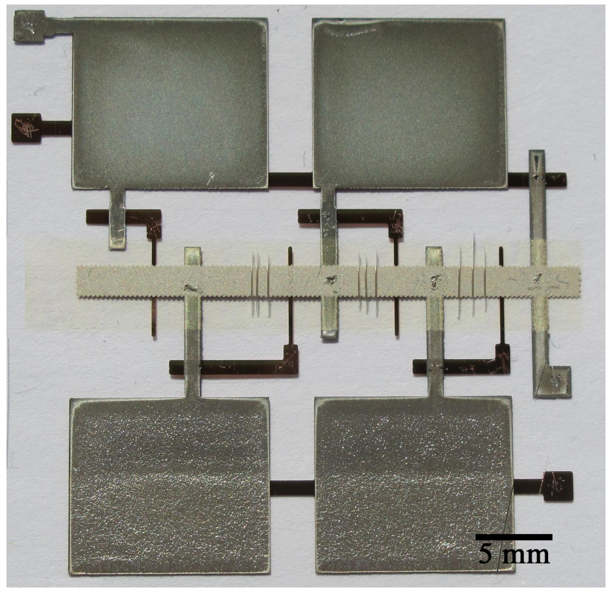


Printed charge pumps

Fabrication

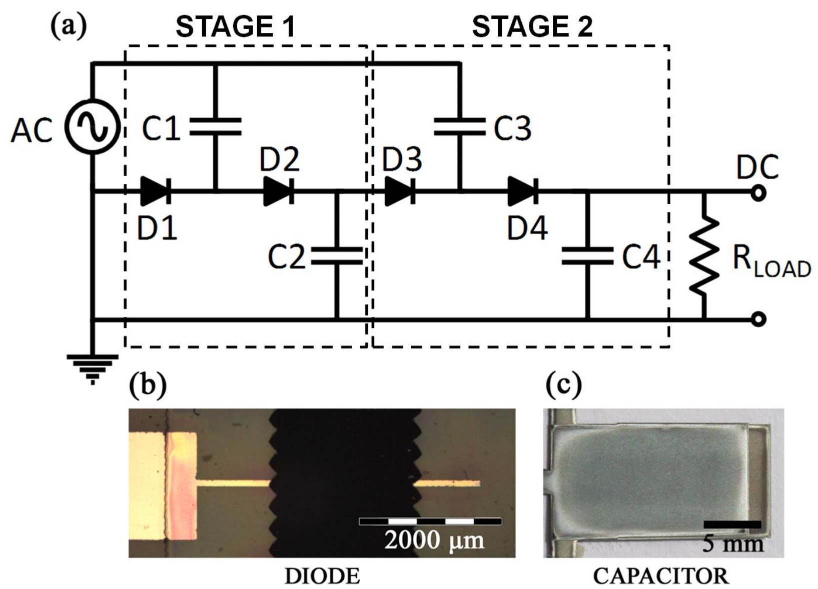
Monolithically integrated printed charge pump

- Printed on a same substrate
- Evaporated Cu electrodes
- Inkjet printed capacitors
  - Dielectric + top electrode
- Gravure printed diodes
- All processing steps in ambient air



Integrated printed charge pump

- Diodes and capacitors printed separately
- Completely inkjet printed capacitors
- Gravure printed diodes
  - Evaporated Cu bottom electrode
- Integrated on printed substrate
- All processing steps in ambient air

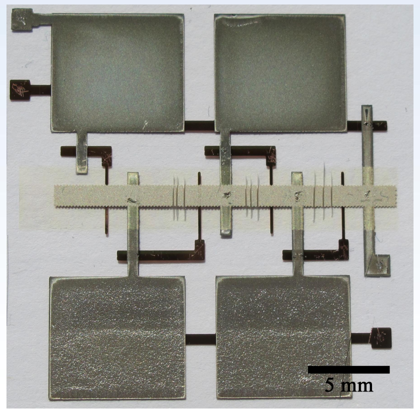


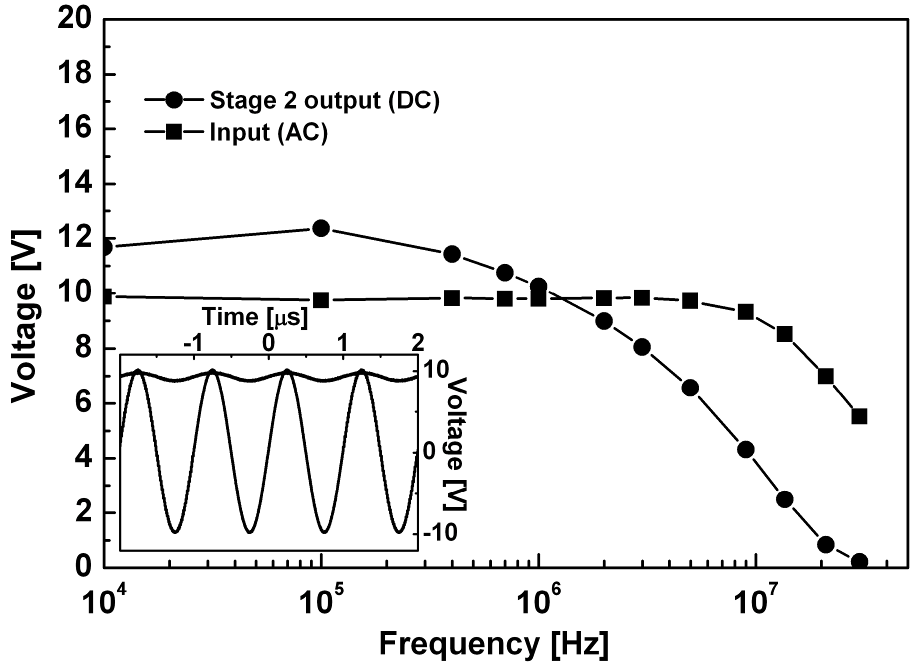
P. Heljo et al., Proc. LOPE-C 2011

Monolithically integrated printed charge pump

Results

- 10 V AC Input amplitude
  - Decreases at high frequencies
  - Capacitive shunting of the diodes
- 1 MΩ load
- Stage 2 output
  - 12.4 V at 100 kHz
- Deterioration of the diode Cu contacts
  - Oxidation during treatments above 70 ºC
  - Variations between diode properties
- Small capacitors
  - Output ripple voltage

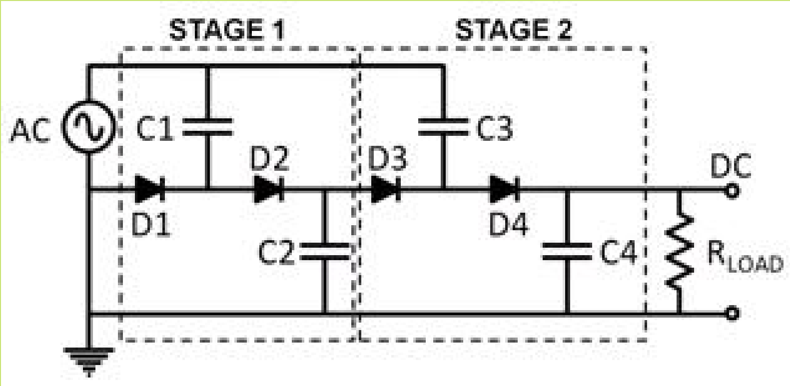




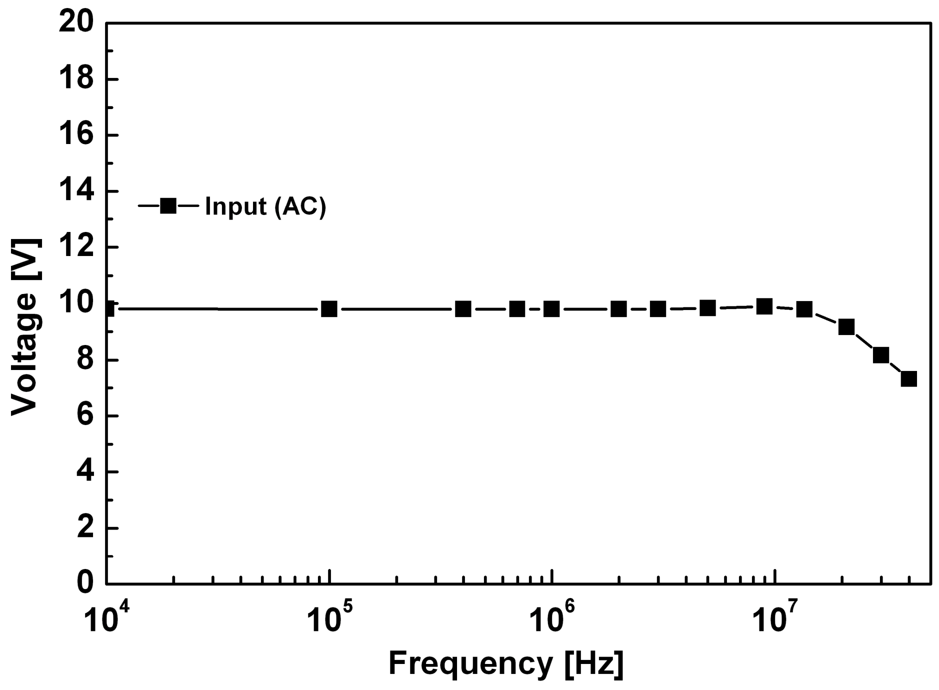
P. Heljo et al., Proc. LOPE-C 2011

Integrated printed charge pump

Results



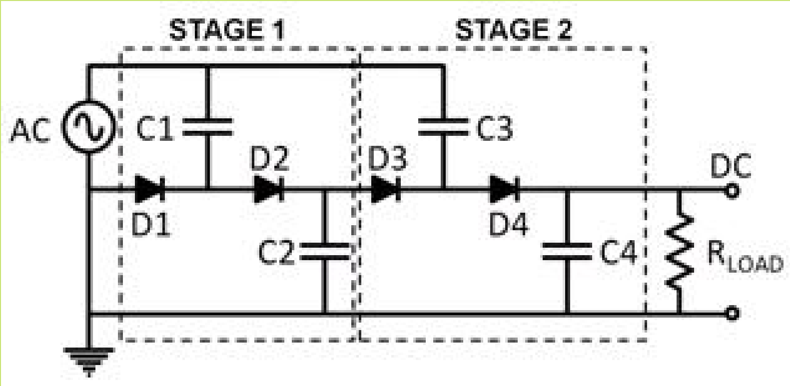
- 10 V AC Input amplitude
  - Decreases at high frequencies
- 1 MΩ load



P. Heljo et al., Proc. LOPE-C 2011

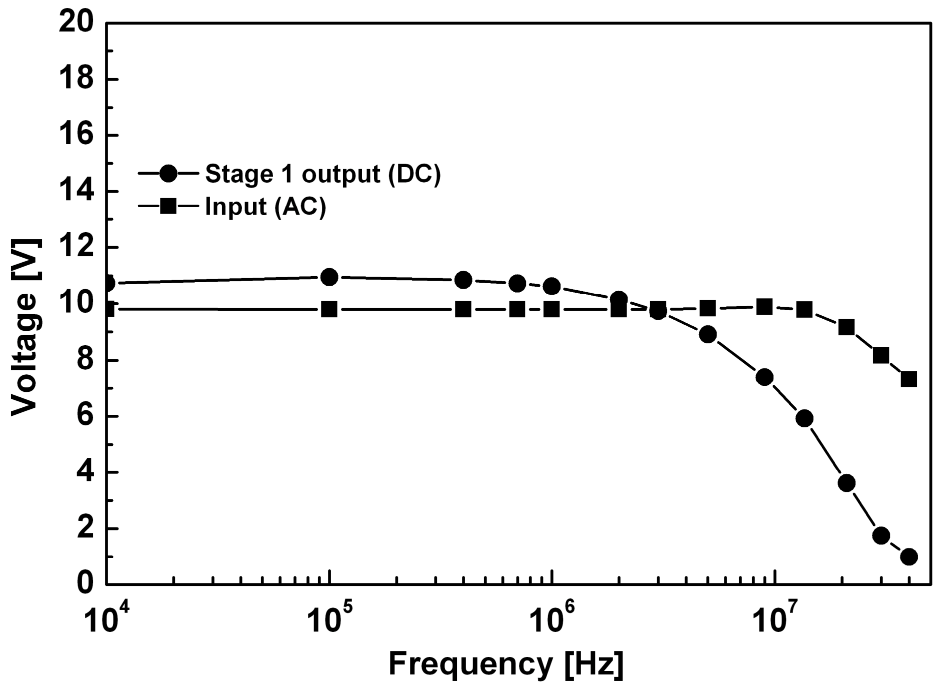
Integrated printed charge pump

Results

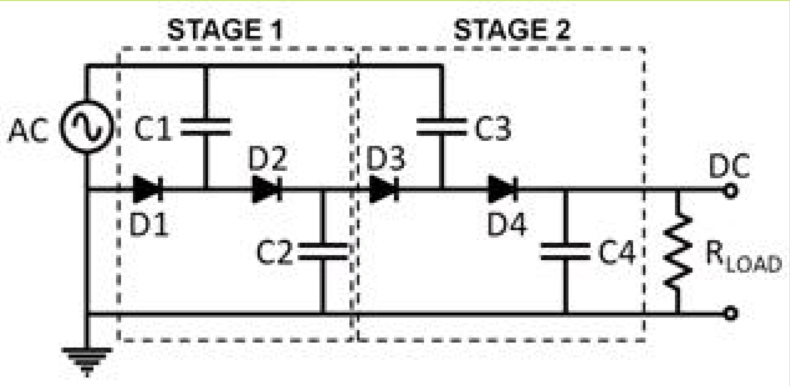


- 10 V AC Input amplitude
  - Decreases at high frequencies
- 1 MΩ load

- Stage 1 output
  - 10.6 V at 1 MHz
  - 5.9 V at 13.56 MHz



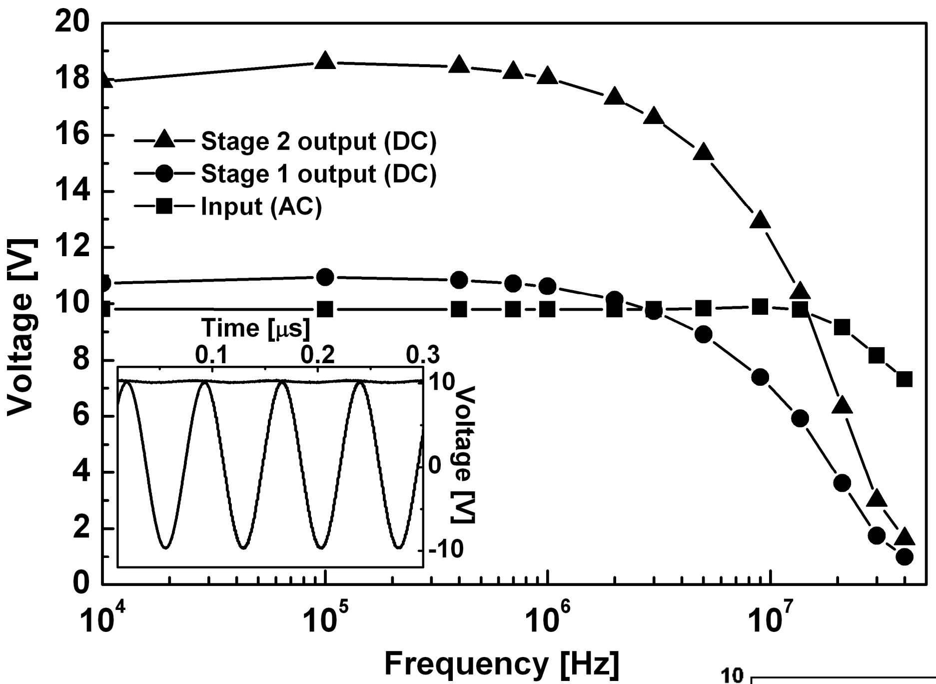
Integrated printed charge pump
Results

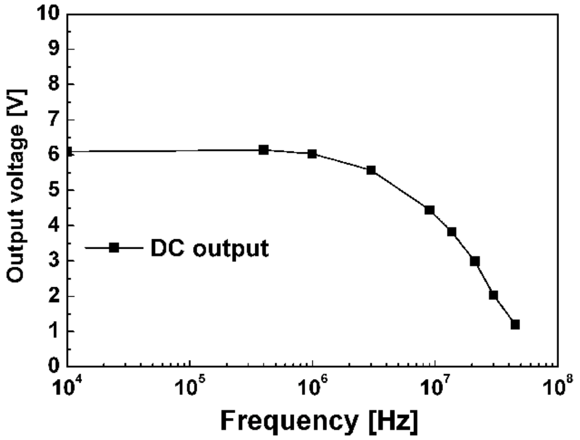


- 10 V AC Input amplitude
  - Decreases at high frequencies
- 1 MΩ load

- Stage 1 output
  - 10.6 V at 1 MHz
  - 5.9 V at 13.56 MHz

- Stage 2 output
  - 18.1 V at 1 MHz
  - 10.4 V at 13.56 MHz
    - 2.7 times the output of a half wave rectifier
  - Low ripple voltage





P. Heljo et al., Proc. LOPE-C 2011

Conclusions – rectifier circuits

- Half-wave rectifier
  - Output voltage is not high enough for many applications
  - Structure, printing and contacts can still be enhanced
  - Better materials
- Benefits of the full-wave rectifier exist at low frequencies
  - Smaller capacitors are sufficient for low ripple voltages
- Charge pump approach for higher output voltages
  - Possibility to add stages with high impedance loads
  - Interesting for many RFID applications
  - Gravure printable charge pumps under development
    - Avoiding the problems with monolithically printed charge pumps
  - Goal is to provide supply voltage for printed transistor circuit

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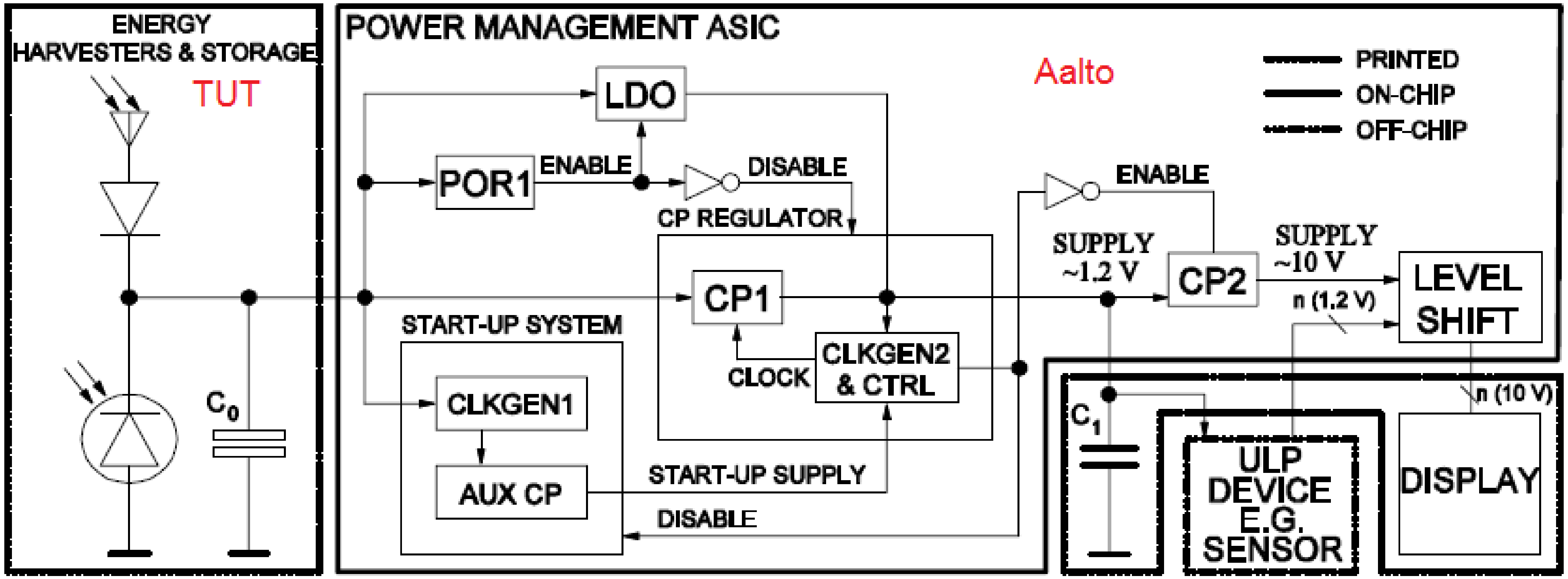
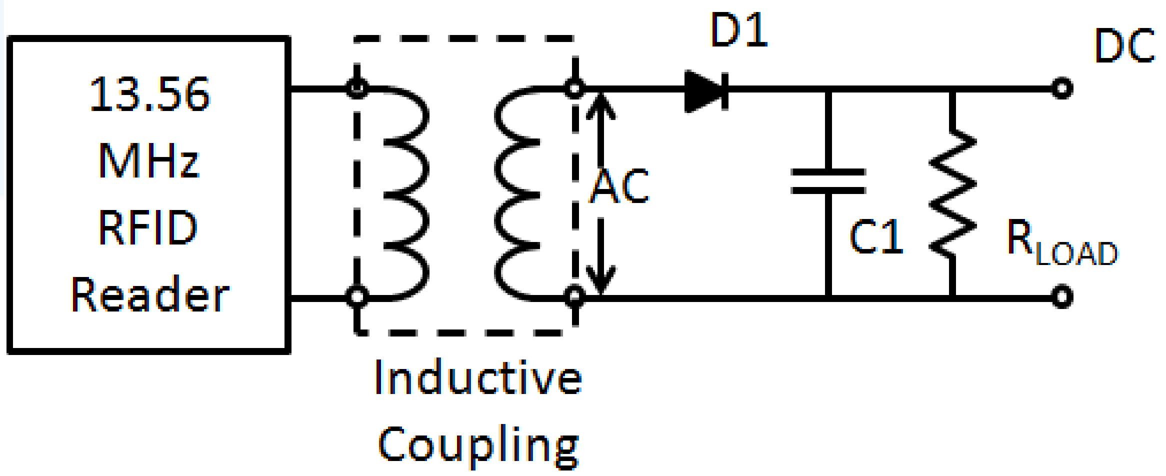
AUTOVOLT Outline

- AUTOVOLT (Universal autonomous power source combining printed energy harvesters and integrated voltage control) - funded by Academy of Finland
- Collaborate with Aalto University
- TUT: RF harvester, solar cell, supercapacitor, integration



Printed RF energy harvesters

- Replace batteries, commonly used in passive RFID tags
- Collect or receive RF energy in a wireless mode (Antenna)
- Provide DC power to a wide range of circuitry (Rectifier: diodes + capacitors)

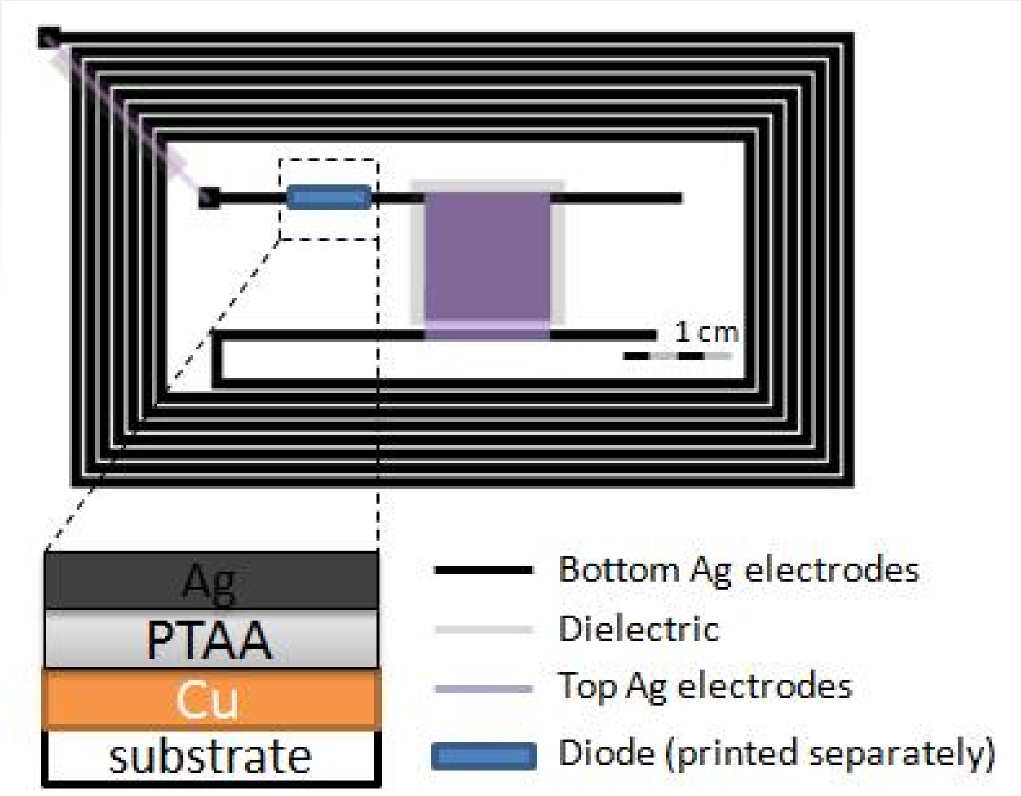


Printed RF energy harvesters

Integrated printed RF harvesters

- Inkjet printed antennas and capacitors
- Gravure printed diodes

- All fabrications were performed in ambient Environment
- The harvester is of the size of a credit card



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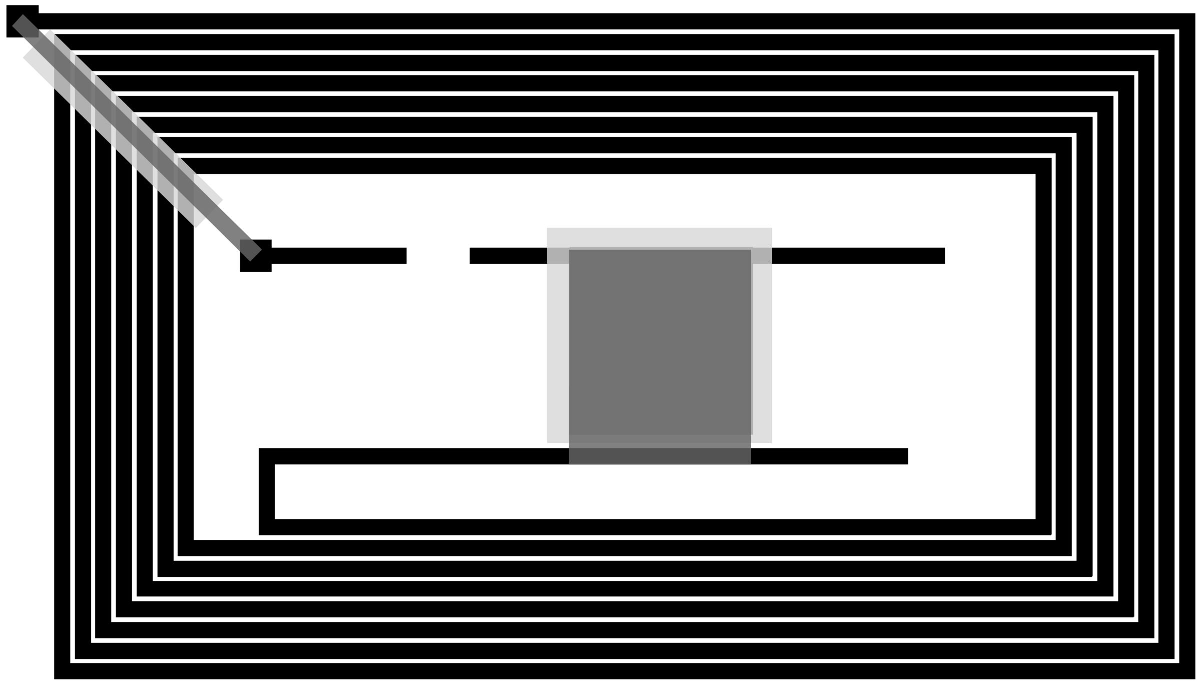
Inkjet printed antennas and capacitors

- Maskless, fast prototyping in circuit development
- Also feasible for manufacturing

iTi MDS 2.0 inkjet printer
- Higher speed, large area deposition

Dimatix DMP-2831 inkjet printer
- Fast, accurate small pattern



- Dielectric ink: SunTonic insulator U5388
- Conductive ink: Harima NPS-JL Silver

- Antenna: 8 turns, total length of 1445 mm
- Capacitor: 1.3 cm^2 , 0.4 nF

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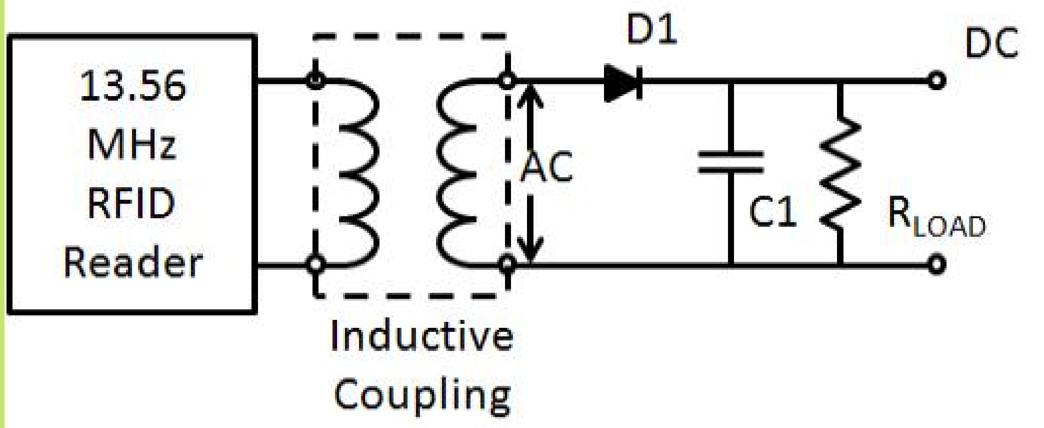
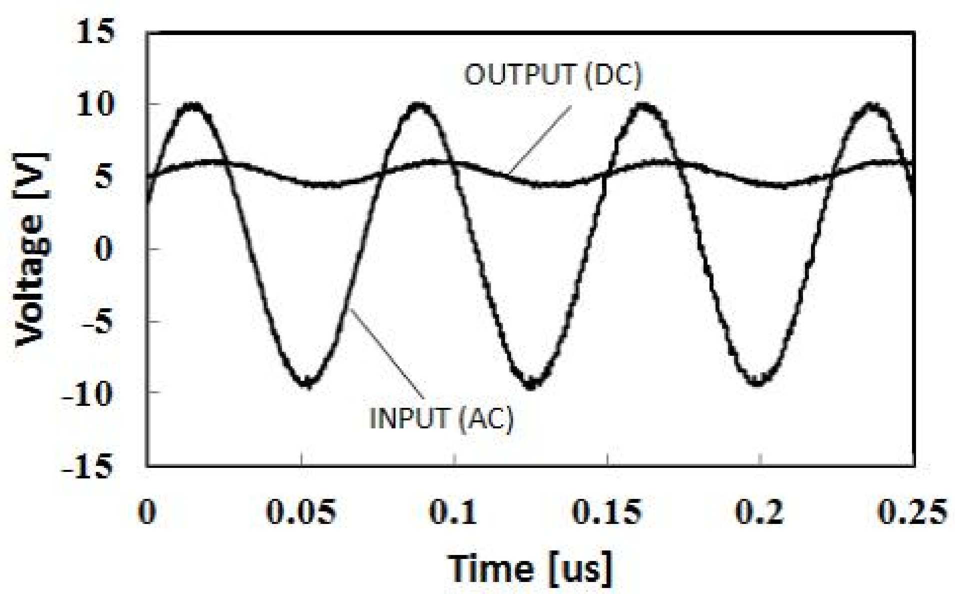
Printed RF harvester

Results



- 10 V coupling AC input amplitude
- 1 MΩ Load
- 13.56 MHz

- Rectifying output: 5 V
- Small ripple



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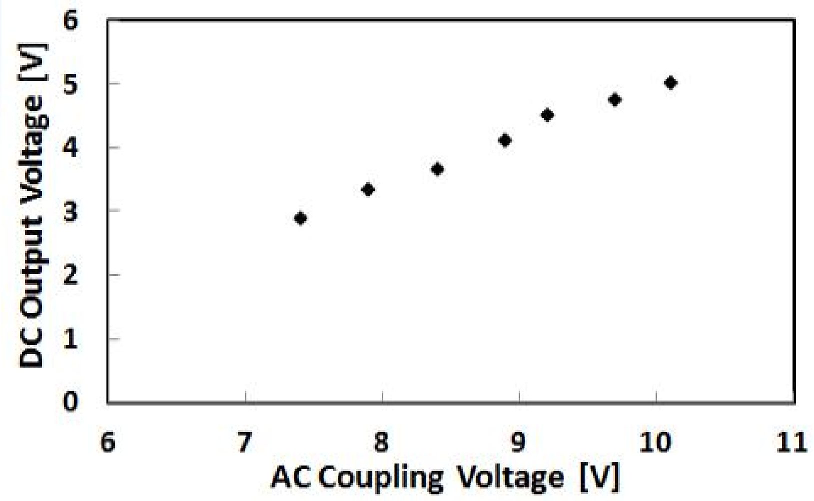
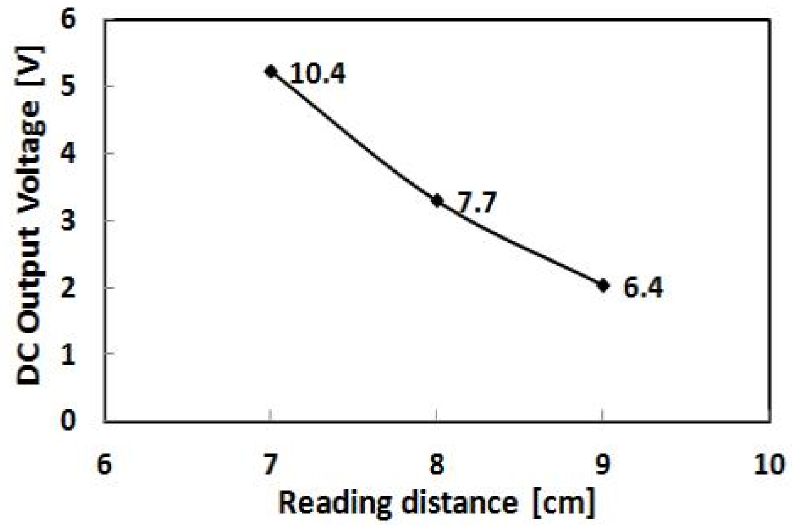
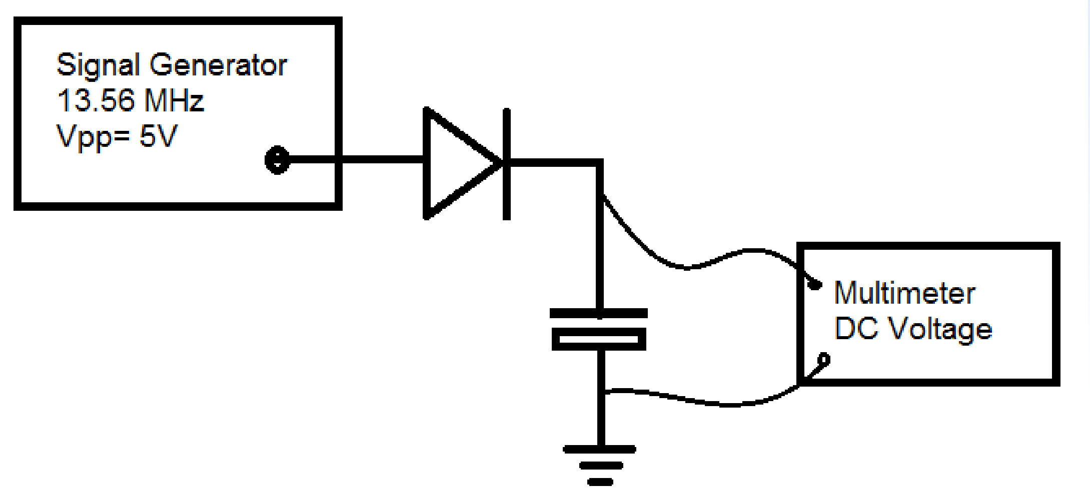
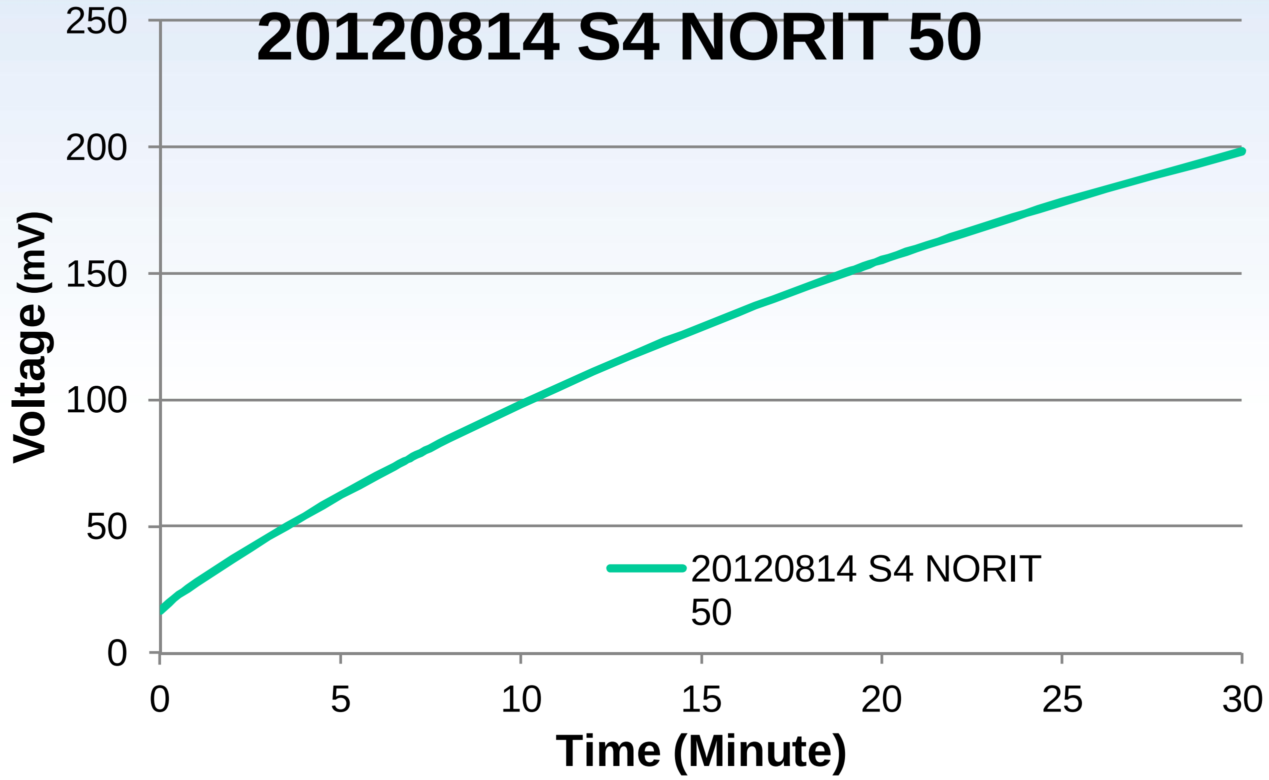
- Varying DC output 3-5 V
  - Changing the transmitting power
  - Adjusting the coupling distance





Initial Tests on Charging Supercapacitors (benchmarking) through Organic Diodes





•Signal generator: Vpp 5V, at 13.56MHz

• Charging rate: 6.056 mV/min
• Discharging: "slowly" discharge itself due to the internal leakage currents, approximately 0.1-0.3mV/min

Conclusions – Energy harvesting

- An RF harvester using organic diodes and optimised antennae can be printed using air stable materials and ambient processing
  - Reduction in the SC thickness improves DC output efficiency
  - DC output of 5 V for 10 V AC coupling input at 13.56 MHz
  - DC outputs of 3-5 V can be provided with the half-wave rectifier configuration
  - Output of an organic diode can be used to charge a supercapacitor for interim power in a printed energy harvesting system, e.g. for operation of a sensor circuit
- Further development is needed
  - Improve organic diode efficiency
  - Optimal load (diode modelling)
  - Integrate different rectifiers/voltage multipliers

Summary and outlook

- Gravure printed Schottky diodes can work quite well – even when they shouldn‘t
- HF rectifier diodes can be printed using a fully air stable amorphous hole conductor polymer and no fine patterning steps
- The right circuit (half wave, full wave, charge pump) depends on the operating frequency and input requirements – and the limits of performance of the organic diodes
- Printed RF rectifier circuits can be used for energy harvesting

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