Solvothermal synthesis of GIZO nanoparticles for solution-processed electrolyte-gated transistors

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Introduction

Solution-processed field-effect transistors are important building blocks in flexible electronics. Nevertheless, many challenges have still to be overcome in order to achieve high-performance transistors. Low temperature, reproducibility, large areas and cost effectiveness are at the present the main concerns.

In this work we developed a electrolyte-gated transistor based on hydrothermal synthesized GIZO nanoparticles dispersed in ethanol with variable amount of ethylene glycol and annealed at 350 and 250 ºC for one hour.

Solid composite polymer electrolyte was based on aqueous dispersions of vinyl acetate stabilized with cellulose derivatives, acrylic acid ester in styrene and lithium perchlorate. Both layers were deposited by spin coating.

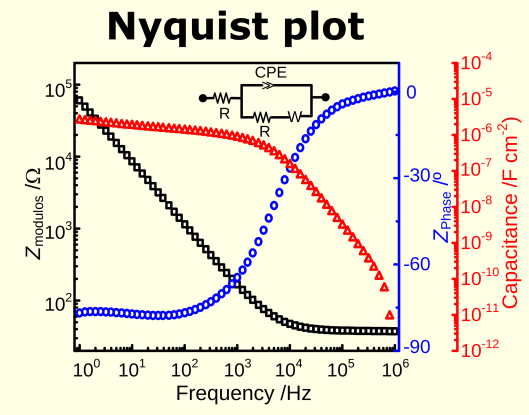
Electrolyte-gated transistors (EGTs) are particularly interesting for nanoparticle based semiconductors as the electrolyte promotes a more efficient coverage of the channel layer besides reducing the working voltage when compared with conventional dielectrics gating.

The operation mechanism of the produced EGTs changed from electric double layer to electrochemical doping by increasing the applied gate voltage range.

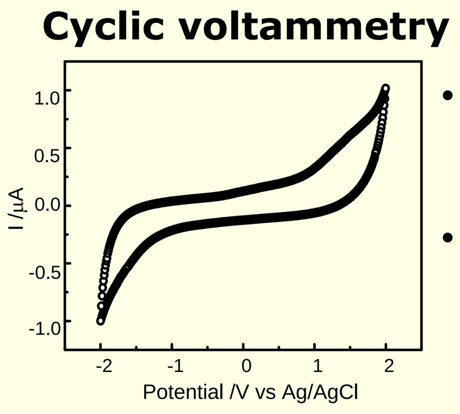
Experimental Section

1. Hydrothermal synthesis of GIZO nanoparticles and ink formulation
2. Semiconductor deposition by spin coating with thermal annealing
3. Composite solid polymer electrolyte deposition by spin coating

Nyquist plot

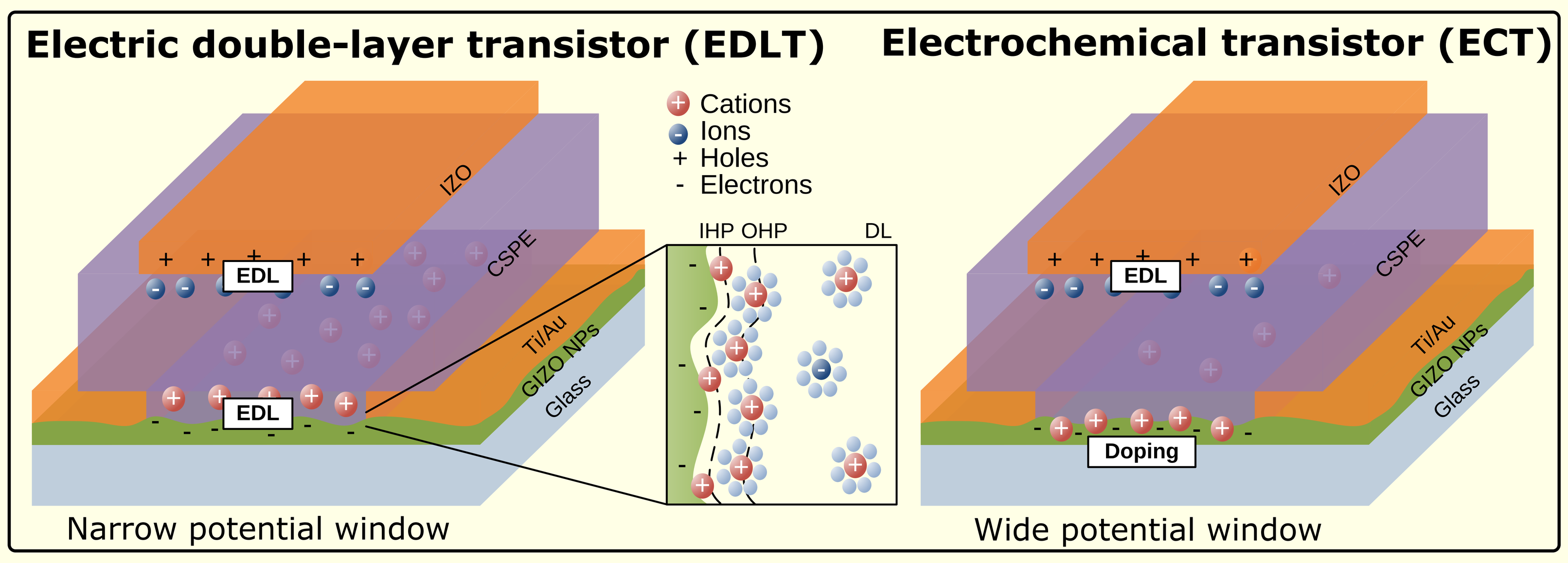


Cyclic voltammetry



- Mainly capacitive current (Au/Electrolyte/Au)
- Capacitance: $C_{DL} = [Y_o R_s^{-(\alpha-1)}]^{1/\alpha}$ $= 0.85\ \mu F/cm^2$

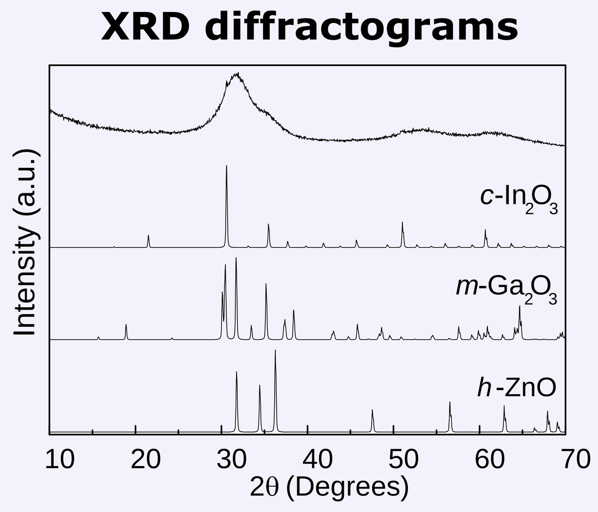
4. TFT assemble (top-gate structure)



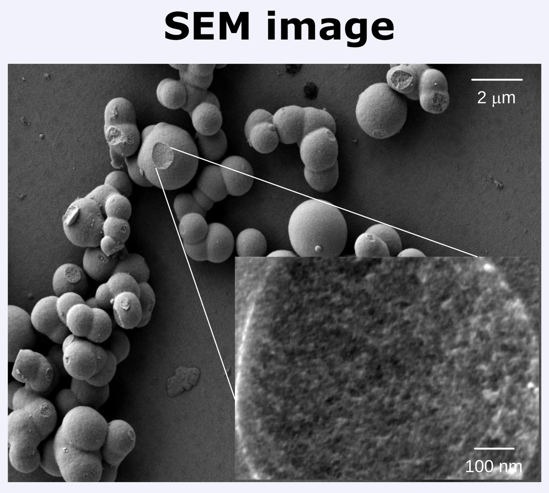
Results and Discussion

1. GIZO NANOPARTICLES

XRD diffractograms

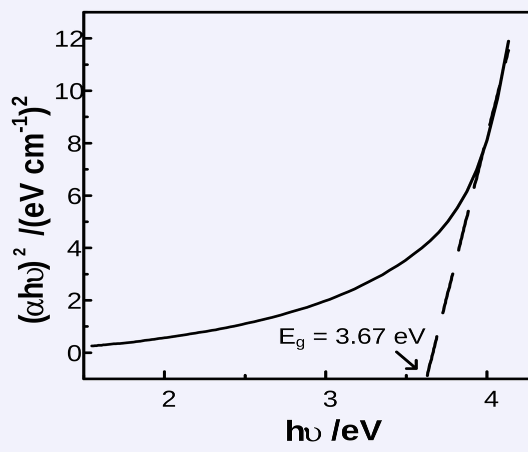


SEM image

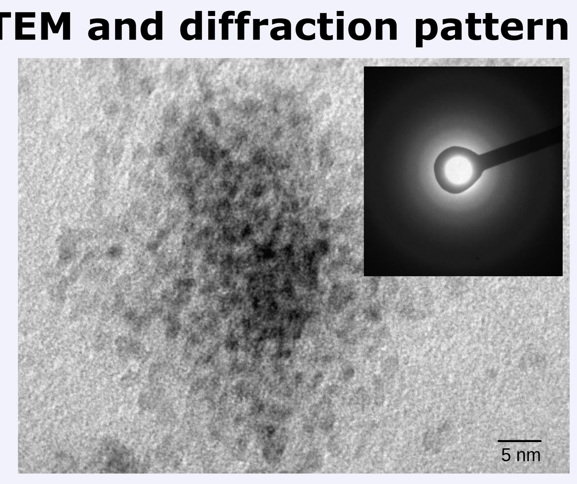


- GIZO nanoparticles are composed of a mixture of 3 oxides.
- EDS analysis: Atomic ratio of Ga:In:Zn - 1.4:4.7:1.

UV-vis spectroscopy



TEM and diffraction pattern



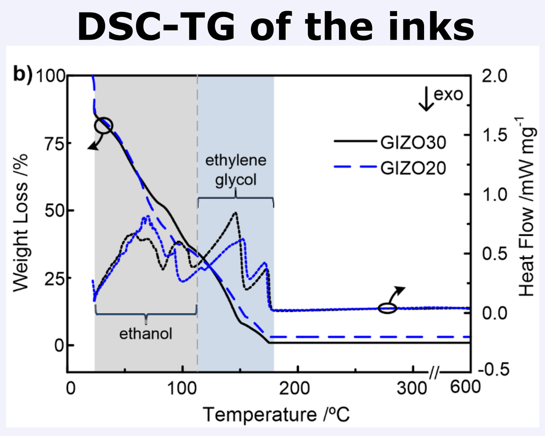
- Wide optical band gap material.
- NPs <5 nm with microsized agglomerates.

2. GIZO THIN-FILM

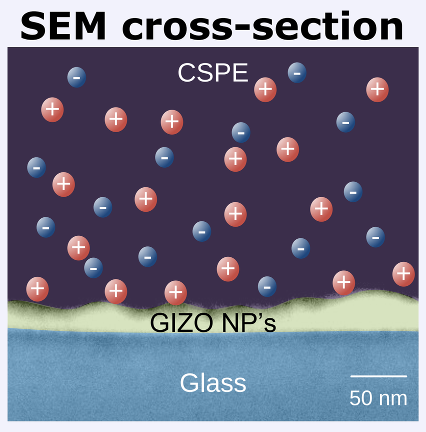
GIZO30 (30 wt.% EG)

GIZO20 (20 wt.% EG)

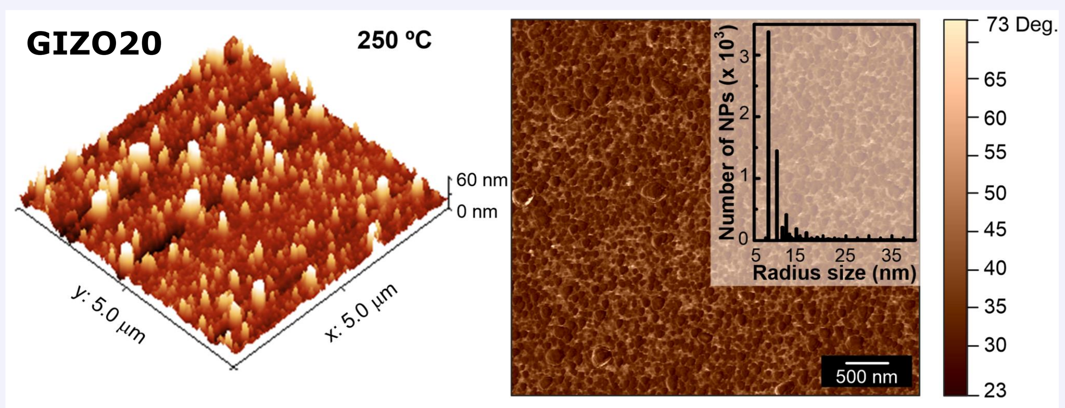
DSC-TG of the inks

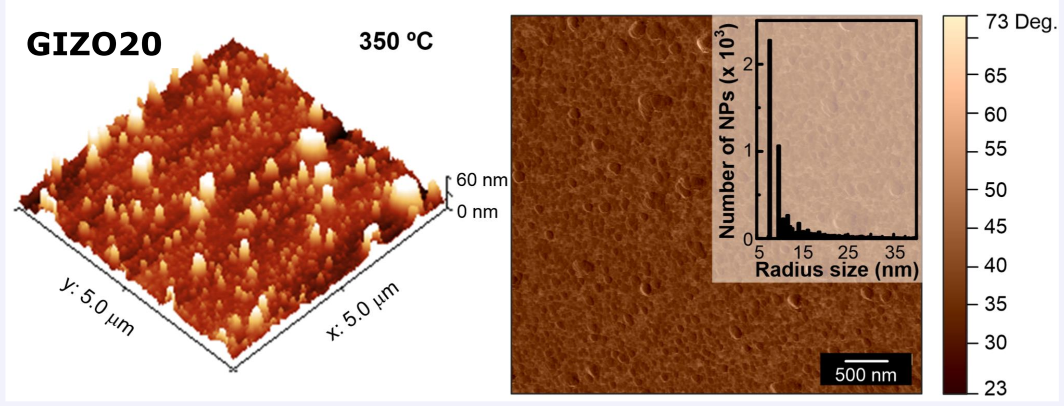


SEM cross-section



AFM – Topography and phase images





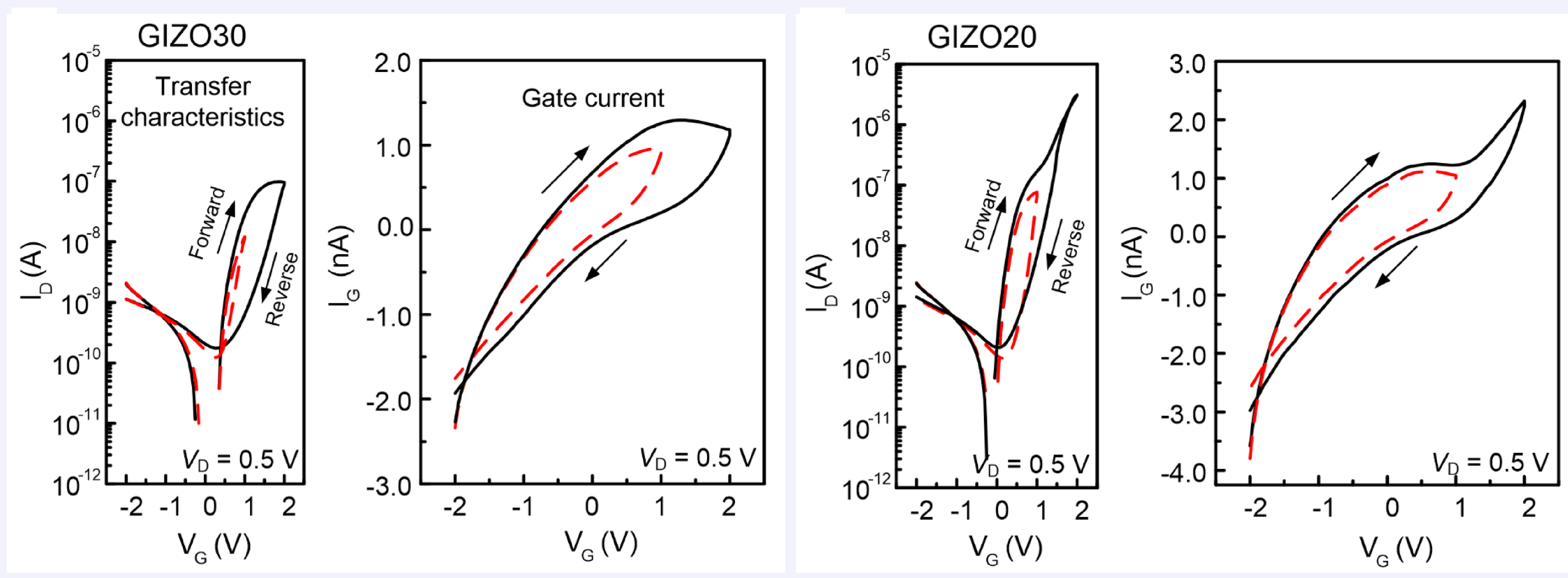
- After 1 hour annealing @ 250 ºC, the ethylene glycol (EG) is still present in the film.
- The film of the ink GIZO30 is thinner than the film of ink GIZO20.

3. EGTs ELECTRICAL CHARACTERIZATION

	Deposition technique	Post-treatment	W/L	I_{ON}/I_{OFF}	V_{Th} (V)	V_D (V)	μ (cm^2/Vs)	SS ($V\ dec^{-1}$)	Ref.
ZnO NR	Drying	150 °C	50	4×10^4	-1	1	5.5	--	1
ZnO NW	Harvesting	--	--	10^7	0.93	0.5	62	0.12	2
ITO	Inkjet printing	400 °C	8	2×10^4	-0.22	0.8	5	--	3
In_2O_3	Inkjet printing	--	12	2×10^3	0.54	0.4	0.8-0.26	--	4
GIZO30				1×10^4	1.6		0.1	0.22	5
GIZO20	Spin coating	250 ºC	35	1×10^5	1.9	1	1	0.24	5
GIZO30				8×10^3	0.7		0.02	0.09	5
GIZO20	Spin coating	350 ºC	15	1×10^6	1.4	0.5	1	0.11	5
GIZO30+				1×10^3	0.6		0.006	0.09	5
GIZO20+	Spin coating	350 ºC	15	5×10^3	0.3	0.5	0.02	0.09	5

+ (Narrow gate voltage range, from -2 to 1 V)

- The electrical characterization of the produced EGTs is comparable with the literature reported above.



- The gate current is capacitive in EDLTs and faradaic in ECTs.
- The operation mechanism alters with the gate potential range.
- EDTs are sensitive to the surface/interface while ECTs to the thickness of the semiconductor.

Conclusions

➢ Solid state electrolyte gated transistors were successfully produced using ternary metal oxide nanoparticles as semiconductor.

➢ Gallium-Zinc-Indium oxide nanoparticles synthesized by hydrothermal synthesis revealed n-type semiconductor properties and produced high quality thin films by spin coating, using ethylene glycol as dispersant.

➢ Best EGT performance was achieved with a I_{ON}/I_{OFF} of 10^6 and a mobility of 1 $cm^2/V.s$. After 6 months the EGTs were still functional but with lower I_{ON}/I_{OFF}.

➢ The annealing temperature was crucial to generate oxygen vacancies in the GIZO film that allowed higher currents, higher mobilities and V_T close to 0 V due to the full degradation of the dispersant (ethylene glycol).

➢ Electrolyte development with higher double-layer capacitance are under development in order to promote a higher mobility and faster response.

➢ This study proves that GIZO nanoparticles can easily be incorporated in EGTs compatible with solution-processed technologies, low cost and flexible devices, demanded for several applications, as flexible electronics and (bio)sensors.

References:

[1] S.Thiemann,M.Gruber, I.Lokteva, J.Hirschmann, M.Halik, J.Zaumseil, *ACS Applied Materials & Interfaces* 5 (**2013**) 1656–62

[2] B.Nasr, D.Wang, R.Kruk, H.Rösner, H.Hahn, S.Dasgupta, *Adv. Funct. Mater* 23 (**2012**) 1750

[3] S. Dasgupta, G. Stoesser, N. Schweikert, R. Hahn, S. Dasgupta, H. Hahn, *Adv. Funct. Mater.* 22 (**2012**) 4909

[4] S. Dasgupta, R. Kruk, N. Mechau, H. Hahn, *ACS Nano* 5 (**2011**) 9628

[5] L. Santos, et al, *ACS Applied Materials Interfaces* 7 (**2015**) 638

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