# Evaluation of upscaling the selective electrophoretic deposition of reduced graphene oxide on miniaturized Au interdigital electrodes from chip- to wafer-level

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## Abstract

Today's novel materials challenge the research industry to enhance the performance and to reduce the power consumption of microchips as well as to develop new sensor principles. All this exerts pressure on the investigation of new economical mass production technologies for the integration into standard process sequences or on top state-of-the-art CMOS devices. Since its discovery in 2004, many different variations of graphene have been investigated. According to Google Scholar Analysis, the number of publications of graphene-based content has grown exponentially from a few in 2004 exponential to 1.2 million only in 2019. However, until today is the deposition of graphene-based materials at wafer-level still difficult to achieve economically reasonable results on standard SEMI wafers up to 8" diameter.

This publication addresses the selective electrophoretic deposition (EPD) of reduced graphene oxide flakes (rGO) on interdigitated gold electrodes. This technique is a very promising deposition method for large scale fabrication, with is based on similar equipment as electroplating for microelectronic production processes. The EPD of rGO particles is the only known way to create 3D-graphene surface topographies for an enhanced sensing area of electrochemical sensor applications, e.g. biosensors. The electrical and chemical properties of this novel material provide a broad range of applications for possible sensor solutions [1, 2]. Firstly, the deposition of rGO is shown on chip scale to gain optimum parameters in suspension preparation and EPD deposition time/voltage for a uniform particle deposition over the sensor area. Shortcuts due to particles between the transmission lines or co-deposition on reference electrodes have to be avoided. This leads to a high selectivity in rGO particle deposition on Au-structures. Hereinafter, a proof of principle for the developed rGO deposition process on extended surface areas is given by experiments on array level and a wafer-level deposition using a low suspension volume.

In previous work, the adhesion of rGO on Au structures in electrochemical sensors with a liquid flow, showed a migration of the deposited particles with the friction of the liquid [3]. Therefore, standard separation of particle agglomeration or splitting of primary particles with ultra-sonic sonotrodes are not sufficient to gain highly concentrated suspensions with homogenous target particle distributions ($< 0{,}5\mu m \leq 1\mu m \geq 5\mu m$). For this reason, a novel particle crushing preparation by ball milling is introduced and enhanced selectivity with an improved adhesion is demonstrated. A full process of the preparation of the colloidal suspension with defined target particle sizes resulting to an optimum zeta potential, will be provided and the cathodic electrophoretic deposition shown [4, 5]. For the evaluation of the deposition experiments, stereo microscopy is used to reveal the selectivity on the interdigital electrode (IDE) structures (sensor area) and scanning electron microscopy (SEM) analysis is used to characterize particle sizes and 3D topography, in terms of primary and secondary particles (agglomerates).

For this study, IDE structures with 15 different geometry variations (3 µm to 15 µm lines and spaces) are used that were manufactured [6] to evaluate the rGO deposition on chip level. A novel multisensory array design with eight sensing areas is presented, combined with wafer-level deposition as a proof of concept on a 200mm SEMI glass wafer.

## Key words

electrophoretic deposition, reduced-graphene-oxide, wafer-level, upscaling, biosensors

# I. Introduction

The integration of novel materials into existing production processes in semiconductor industry is always challenging, even though the materials have been discovered almost two decades ago, like the promising material graphene. “It may be the most amazing and versatile substance available to mankind.”, according to the Graphene Flagship Project, funded by the European Union. This material is in its basic properties only 1 atom thick, stronger than steel or diamond, flexible, transparent, ultra-light and thermally, as well as electrically conductive. In its oxidized form, it is insulating, which reveals similar behavior to silicon. These properties impede the integration into processes of wafer-level semiconductor fabrications. The deposition with liquid phase exfoliation, chemical vapor deposition or mechanical exfoliation is very promising, but still in a very small scale applicable. Depositions on 4” to 6” as well as on 8” wafers have been shown in lab environment, but no commercial process on larger scale with a good reproducibility and minimal defects has been found yet [13].
In this work, the used material is reduced graphene oxide (rGO). These are multilayer graphene flakes, which were oxidized, and thermally reduced by the manufacturer, to gain functional, chemical groups for sensor applications with a good electrical conductivity. These flakes are easier to integrate into wafer-level fabrication processes like the EPD technique shown in this work.

# II. State of the art process

## *A. Basic principle of EPD*

Electrophoretic deposition technique is a simple electrochemical method to deposit non-metal particles on metal surfaces. It is well known in the automotive sector with cathodic dip coating for the preservation of car parts against corrosion. Therefore, the shape of the substrate can vary and does not have to be planar. Other advantages are the relatively simple deposition instruments and the relatively fast deposition times at low cost. The scalability of this process and the use of a variety of different materials is the main motivation for this work. EPD can be divided into four steps [1] according to Figure. 1.:

1. The first step is the production of the dispersion, known as the colloidal suspension. Randomly charged particles are dissolved in an electrolyte, with different sizes and shapes. The influencing parameters in this step are the initial particle sizes, the concentration of particles and the choice of the electrolyte (aqueous, solvent, etc.). Treatments to change the properties of particle size distributions like stirring, ultra-sonification or other particle crushing methods are applied.
2. In the second step, the particles are charged with additives, to gain a stable suspension with colloidal, uniformly charged particles. The Zeta-Potential, also known as the kinetic surface potential, is a critical parameter in this step. The higher it is, the better is the suspension stability against sedimentation and agglomeration, the higher is the mobility of the particles within the electric field during electrophoresis [7;8].
3. The electrophoresis describes the movement of particles through the Coulomb force in the suspension with an induced electric field between an anode and a cathode. [1;9;10]. Particles migrate to the oppositely charged electrode. If positively charged particles migrate to the negatively charged electrode, the deposition is called cathodic electrophoretic deposition. On the other hand, if the negatively charged particles migrate to the positively charged electrode, one speaks of anodic deposition. [11]
4. In the last step, the nano-/micro-sized colloidal particles will deposit on the electrode surface with Van-der-Waals interactions and agglomerations by stacking layers [12].

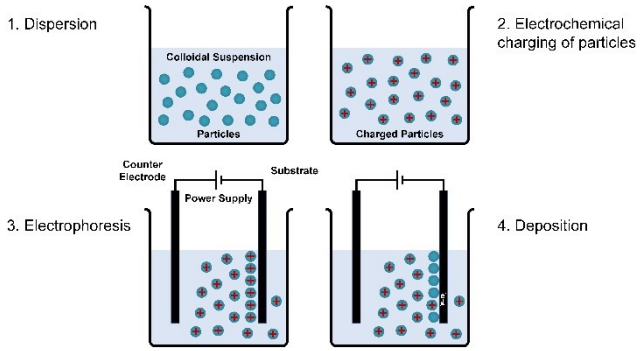


*Figure 1: Process steps of EPD [4]*

In the following section, the first evaluations and results of the initial deposition method with occurred effects will be shown.

## *B. Initial, non-optimized process*

The initial process has been developed in previous work [2] and will be described in the following according to the four steps of EPD.

1. Dispersion preparation (US-Sonotrode):

30 mg of rGO-NH2 particles purchased by the company NanoInnova Technologies SL are dissolved in 20 ml of 2-propanol (non-aqueous). The dissolving takes place in inert gas atmosphere, using glove boxes, because of safety reasons by handling nanoparticles. Afterwards, the cup with the dispersion is placed in an ice-water bath for cooling the dispersion during ultra-sonic treatment. The treatment method will separate agglomerated prime particles and helps for a better distribution in the electrolyte. Therefore, the sonotrode with a diameter of 20 mm and a maximum power of 200 W is placed just 5 mm into the dispersion. A magnetic stirrer is placed in the ice bath as well as one in the dispersion. In total, three steps of ultra-sonic treatment are applied with cooling breaks in between according to Table 1.

*Table 1: Ultra-sonic treatment for particle separation*

| Step | Time | Pulse | Amplitude |
|---|---|---|---|
| **1** | 20 min | 20 % | 80 % |
| **2** | 5 min | 0 % | 0 % |
| **3** | 30 min | 10 % | 75 % |
| **4** | 5 min | 0 % | 0 % |
| **5** | 40 min | 10 % | 70 % |
| **6** | 5 min | 0 % | 0 % |

At the end of the treatment, another 20 ml of 2-propanol are added into the dispersion.

2. Electrochemical charging and particle size filtering:

A concentration of 46 µg/ml $MgCl_2$ is dissolved in 2-propanol. From this solution, 1.5 ml are added to the dispersion. With this concentration of MgCl2, a zeta-potential of 39 mV was measured. Afterwards, step 5 and 6 of Table 1 will be repeated.

In order to gain a maximum desired particle size, the dispersion will be centrifuged and filtered with a 5 µm syringe filter. Close before the deposition takes place, step 5 and 6 of Table 1 will be repeated again.

3. Electrophoresis:

Before the electrophoresis takes place, the sensors (ED-IDE3-Au from MICRUX FLUIDIC S.L. – Au-electrodes with 5 µm lines and space) will be plasma activated with an oxygen plasma for the cleaning of the surface and to gain a high hydrophilic surface energy.

Figure 2 shows the EPD setup. The counter electrode is a silicon die coated with a sputtered Au layer connected as anode. The pads of the plasma activated sensor chip are connected to the cathode. Therefore, the EPD mechanism is a cathodic deposition. The distance between the electrodes is 1 cm. Before the electrophoresis starts, the dispersion will be stirred, to wet the electrode surface for one minute. Afterwards the stirring will be stopped and a voltage of 100 V will be applied for 120 s. [1;2] A migration of particles to the cathode can be observed.

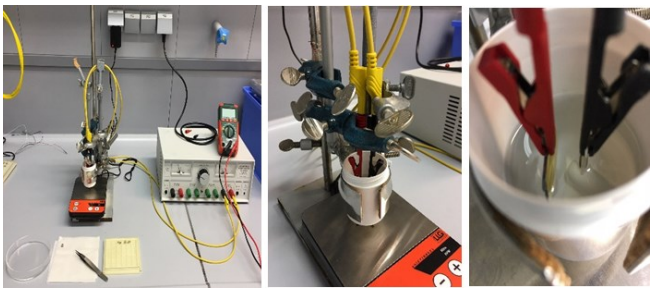

*Figure 2: Initial EPD setup (from left to right: Full setup with stirrer and power supply / Stirrer with cup and connection cables / Counter electrode (anode) and sensor (cathode) in almost transparent dispersion)*

4. Deposition and result

After the deposition took place, the sensor chip will be washed in clean 2-propanol for 3 min on a magnetic stirrer. A baking in a vacuum furnace at 100°C for 6 hours is done at the end. Figure 3 compares one IDE-chip prior to EPD (left hand side pictures) and after deposition (right hand side pictures). The microscope images on top show the rough rGO-occupied electrode surface in the non-passivated sensor area (top right), in comparison to the blank die (top left). The images below show a close-up view of the IDE taken by SEM and prove a clean, shortage-free deposition of the electrodes by rGO particles.

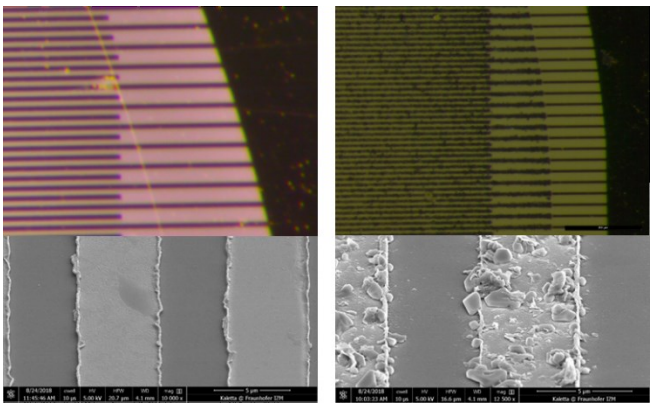

*Figure 3: Microscope image (top) and SEM image (bottom) of before EPD (left) and after EPD (right) of rGO*

*Observations:*

Due to the low concentration of particles in the dispersion, and because of the lower electrical conductivity of the rGO-$NH_2$ material, the deposition voltage is relatively high and not applicable in aqueous electrolyte. After the deposition of a maximum of 5 dies, the rGO concentration in the dispersion is already depleted. The time of sedimentation of the dispersion is only 2 days. This leads to the assumption that the instability of the dispersion is due to the low rGO concentration. There is not enough repulsion between the similarly charged particles to keep them in movement.

After the deposition it can be observed, that a higher amount of particles is deposited on the edge of the sensor area and a

depletion can be seen in the center. This leads to a non-uniform deposition on chip-level.
During electrochemical measurements in a fluidic cell, a loss of the adhesion of particles on sensor surface occurred, and resulted in a particle loss due to liquid flow (Figure 4).

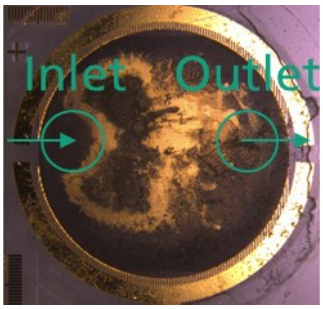


*Figure 4: Adhesion test in flow-cell with inlet and outlet*

Novel sensors with a similar sensor surface for better electrochemical performance have been manufactured [6] and the EPD process has been optimized for a better uniformity, improved adhesion and longtime stable dispersion, described in the following section.

## III. Novel preparation process of dispersion

The main difference to the initial process of the optimized EPD is the preparation of the dispersion. In comparison to the ultra-sonic sonotrode, a ball-mill creates more impacts to separate agglomerations and even separate prime particles, which results in more particles with smaller diameters. In the following, the optimized EPD will be described according to the four steps of deposition.

1. Dispersion preparation (Ball-Mill):

The concentration and dissolvement of the rGO is equal to the initial method. 20 ml of non-aqueous 2-propanol is mixed with 30 mg of rGO (SE1430 from The Sixth Element Inc.) and filled into the ball milling cup of the ball mill Retsch Emax. 50 g of stainless-steel balls with a diameter of 5 mm are filled into the cup. The target particle size is known to be 1/1000 of the ball size. For the maximum number of impacts, the ball milling treatment is a sequence of periodic milling and cooling in 14 cycles with 15 min of milling and 45 min of cooling. The milling takes place at 1800 rpm to crush the particles to a peak particle size distribution of 5 µm. This routine is done over night and in the morning one period of the sequence will be repeated activate the dilution before the removal of the balls and the refilling of the dispersion into a cup with another 20 ml of 2-propanol. The centrifuge treatment and a two-stage filtering has been done at this point. A 10 µm syringe filter is used in the first stage and a 5 µm in the second. As a positive effect, can be seen, that the dispersion is not grey and transparent as the initial method after filtering, it is deep black without any transparency. This indicates an extremely high rGO concentration in the dispersion.

2. Electrochemical charging

Zeta-potential measurements with the Malvern Panalytical Zetasizer Nano ZS and different dilutions of the charging salt concentrations of $MgCl_2$ added to the dispersion, showed a maximum zeta-potential of 40 mV by adding 1.5 ml of a 0,5 mg/ml $MgCl_2$ / 2-propanol solution to the stock dispersion.

3. Electrophoresis

Firstly, the chips are activated by O2 plasma before the contact with the dispersion. As a process optimization, a 3D-printed lid with two PCB connectors for the electrical connection of the electrodes was manufactured (Figure 5). This lid provides for a parallel arrangement and a well-defined distance of 10 mm between the electrodes. As the counter electrode, a chip having the same design as the chip to be deposited is used, to generate a well-balanced electric field. Due to the highly positive zeta potential, the deposition mechanism is cathodic. The necessary deposition voltage is compared to the initial process almost ten times lower, because of the better electrical conductivity of the rGO material as well due to the higher particle concentration in the dispersion. The measured deposition current is less than 60 µA at 15 V for a single die. Multiple results at different deposition voltages and times will be shown in section IV. The deposition current decreases during the deposition time.

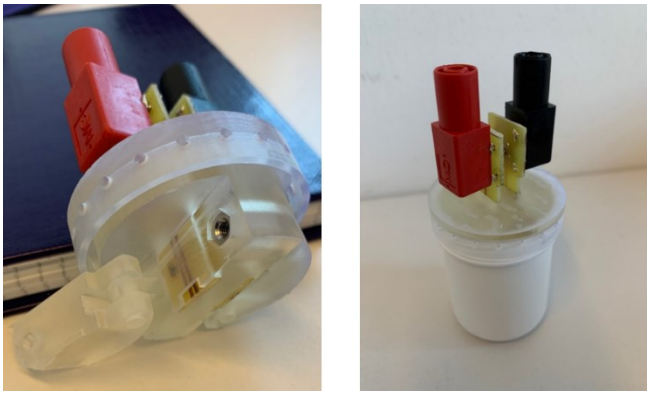

*Figure 5: Optimized 3D-printed EPD fixture for the contacting by clamping two single chips as cathode and anode face to face parallel to each other*

4. Deposition

The post treatment after deposition is equal to the initial process by cleaning/washing and vacuum furnace treatment.

In the following section the results on chip-level will be presented. Finding the sweet spot with a DOE of multiple parameters took 125 experiments. The first dispersion is still stable without sedimentation neither agglomeration since March 2021.

## IV. Deposition on chip level - results

With the new chip design, manufactured in previous work [6], lines and spaces of 10 µm width and 10 µm space of interdigitated electrodes were manufactured. In Figure 6 microscopic images and SEM investigations of rGO deposition with the same voltage but different deposition times can be seen.

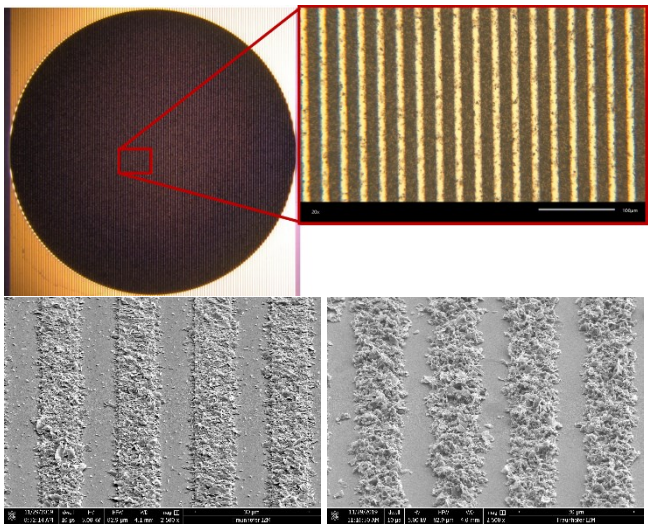

*Figure 6: Left: 15 V and 60 s deposition parameters, Right and top: 15 V and 90 s deposition parameters – 10 µm lines and spaces*

In a liquid flow cell, no loss of particles can be observed. This is an indicator for a good adhesion on the Au-sensor structures. To define the specific deposition, another method to the microscopy is the electrical measurement between the two interdigitated electrodes of the sensor. If a short by rGO particles occurs, the insulation resistance would decrease from the mega ohm range down to 3-10 Ohm. This also indicates the exceptional electrical conductivity of the rGO material.

## V. Deposition on array level

For the upscaling, two different array designs with 8 sensor surfaces in each design, have been developed and manufactured (Figure 7). The two inner pads are shorted by a transmission line, connected to the larger pads on the right. The short on every pad connected to the horizontal transmission line can be opened via laser cutting.

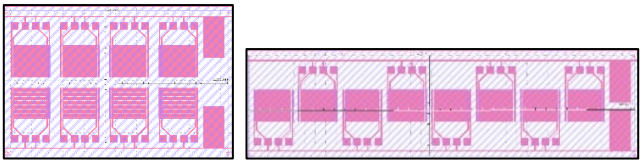

*Figure 7: Sensor-Array layout of 2x4 design and 1x8 design*

For the EPD on array-level, an electrolyte volume of two single chip deposition lots has been produced with an 80 ml total dispersion volume.
In the following Figure 8, microscope images are stitched together to see the difference before and after the rGO deposition in the square sensor surfaces. The sensor areas closest to the large pads have a non-uniformly deposited rGO-film due to a poor wetting close to the electrolyte surface. The electrical connection has been done with alligator clamps equally to the initial EPD setup. The deposition parameters are similar to the chip-level deposition with the only difference in the measured deposition current. The current is 10 times higher at about 500 µA due to the larger deposition area.

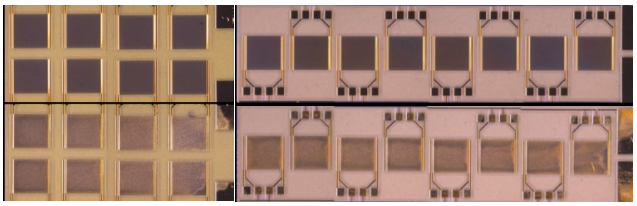

*Figure 8: Left: 2x4 array, Right: 1x8 array, Top: before deposition, Bottom: after deposition of rGO*

## VI. Proof of principle deposition on wafer-level

With the creation of the wafer with the array designs, the wafer-level deposition can be realized. A 4 mm ring contact on the wafer frame can be used to gain a potential on every single IDC structure on the wafer.
For the EPD on wafer-level four times the volume of the initial 40 ml was produced in two days. A total volume of 160ml has been used to realize a deposition. The smallest usual volume for galvanic/electro plating processes in research grade on 200 mm wafer sizes is around 800 ml. Therefore, the EPD in this process is a very low electrolyte volume deposition.
The setup is due to a missing low electrolyte EPD cell with a ring electrode, very simple. A fully Au-coated 200 mm silicon wafer is placed face up as counter electrode (anode) in a low form laboratory glass beaker. The electrical connection on the edge of the wafers have been done with PCIe connectors, soldered to a cable. In between the wafers are three 2.5 mm high PTFE cylinders with a diameter of 5 mm placed, to keep the parallel distance between the electrodes. Afterwards the dispersion will be filled into the glass beaker on top of the counter electrode. The sensor wafer will be plasma activated and afterwards placed face down on top of the counter electrode into the electrolyte. Though the glass substrate, possible trapped air bubbles can be seen and a repositioning can be done. A schematic of the setup can be seen in Figure 9.
With the electrophoresis the particles start to move upwards to the cathode. In principle, no sedimented, larger, agglomerated particles can sink on the sensor surfaces. The observed deposition current on wafer-level was 5 mA, so

again, almost 10x higher than the deposition on array-level and 100x higher as chip-level deposition.

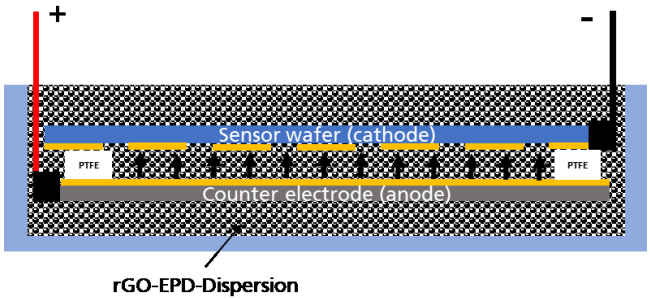


*Figure 9: Schematic of wafer-level EPD setup*

As a result, Figure 10 shows the rGO coated 200 mm glass wafer. It can be clearly seen, that because of the one-point electrical connection (blue on the right) higher electric field strength occurs and decreases to the opposite direction due to the Au metal layer sheet resistance. A better uniformity could be achieved with a ring formed electrode.

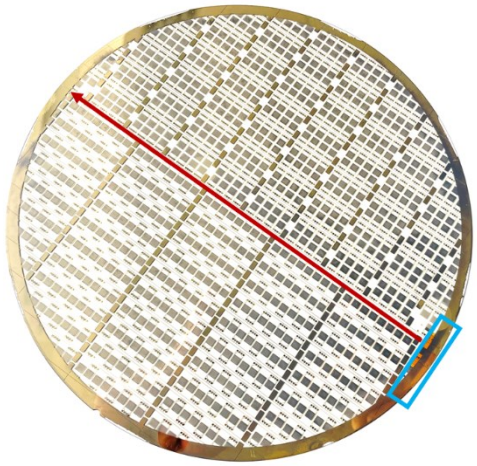

*Figure 10: Result of wafer-level EPD of rGO*

## VII. Conclusion and outlook

In this work, a step-by-step upscaling from die- to 200 mm wafer-level of the electrophoretic deposition of reduced graphene oxide particles has been shown. On chip scale, the dispersion preparation with materials from various manufactures with different properties has been developed and optimized by ball milling to gain a good particle distribution thus a uniform, selective deposition on the sensor structures. These results have been used for a deposition on array level which revealed a similar deposition quality to the chip level results. The proof of principle deposition on wafer-level has been demonstrated. Therefore, the use of EPD in comparison to standard galvanic/electroplating processes in microelectronics is implementable for mass production purposes. Here more work will be done, with a novel low electrolyte EPD cell, with a ring electrode and different variations of the counter electrode design to achieve a perfect arrangement of rGO particles on the miniaturized sensor structures over the full wafer.

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