Study of UV-light induced conductance switching behavior in titanium dioxide based devices

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Abstract I

Nowadays, digital imaging technology plays a more and more important role in social life, pervading different fields of application going from industrial quality control to medical diagnosis, from environmental monitoring to entertainment and homeland security. However, in some imaging applications a large size of the object has to be imaged and sometimes light focusing is either not possible or not convenient. In this case, large area panels are inherently required.

Silicon, which is traditionally used in electronics, is ill-suited to the production of large area panels, because cost would be prohibitive. Solution processable semiconductors might be an interesting alternative, as they can be deposited by scalable printing techniques (roll-to-roll, screen printing, inkjet printing) over large surfaces in a cost effective way.

From the point of view of the working principle, digital imagers typically exploit photodiodes as the photosentitive devices. In this case, light stimulation is translated into photogenerated charges that need to stay stored on the photodiode intrinsic capacitance until the moment the pixel is actually read. An addressing element, i.e. a transistor, is then required for each pixel to provide controlled and selective access to the photodiode (active matrix configuration). Besides some general drawbacks like the fact that the information is transitory and reading is a destructive operation, this solution also shows some difficulties specific to printed electronics, namely: i) integration of different devices (i.e. a photodiode and a transistor) by printing techniques is not trivial; ii) the spatial resolution for printed devices is poor, which means that the transistor will occupy a significant portion of the pixel area at the detriment of the fill- factor.

Here we propose a different approach: imaging pixels based on UV-light induced conductance switching in titanium dioxide (TiO_2). The basic idea is: the transistor would not be necessary if instead the optical information would be translated into a stable variation of electrical parameter (the conductivity) of the photosensitive member. We therefore exploit a well known phenomenon in TiO_2 that results into a light induced n-doping of the semiconductor due to oxygen atoms expulsion from

the material's surface. This translates into a change of material conductivity, containing the required information about the incoming light stimulus.

In this thesis work, after briefly introducing the context (Chapter 1), we will discuss deeply the technology of using such imaging pixels (working principle, fabrication, states of the art) (Chapter 2).

In Chapter 3 we will show that a range of UV-light induced conductance change of more than three orders of magnitude can be obtained for such pixels operated in an inert athmosphere. We will also demonstrate that after light stimulation, good control over pixels spontaneous return to initial conductivity level can be obtained by playing with device fabrication protocol, namely by passivating or not the surface of the semiconductor right after the deposition.

Previous works have shown such kind of pixels can work properly in high vacuum athmosphere, where oxygen atoms expelled upon illumination are not expected to be recovered and the photodoping effect is supposed to be permanent.

In Chapter 4, we show that such pixels can effectively be operated in different working athmosphere as long as air (oxygen, moisture) content is negligible. This represents a crucial step from a technological point of view. Finally we also tested the device for multi cycles to determine whether the pixels can be operated many times, regardless the specific working athmosphere in use.

Finally, in Chapter 5 we will resume on the main experimental results and draw the conclusions.

Abstract II

Al giorno d'oggi, l'imaging digitale è una tecnologia che ricopre un ruolo sempre più importante nella vita quotidiana, trovando applicazione in numerosi settori che vanno dalla diagnostica medica al controllo di qualità industriale, dal monitoraggio ambientale alla sicurezza interna. Tuttavia, a volte gli oggetti di cui si vuole registrare l'immagine hanno dimensioni non trascurabili, e non sempre la focalizzazione del segnale ottico è possibile o semplice da realizzare. In questi casi, è necessario che i pannelli utilizzati per l'applicazione di imaging siano essi stessi di dimensioni non trascurabili.

Il silicio, materiale principe per l'elettronica, non si presta a questo tipo di situazioni, poiché i costi di fabbricazione diventano proibitivi. In alternativa, si può pensare di ricorrere a semiconduttori che siano processabili da soluzione, magari attraverso tecniche di stampa scalabili e a basso costo, quali inkjet printing, screen printing, tecniche roll-to-roll.

Da un punto di vista del principio di funzionamento, gli imager digitali utilizzano spesso come elementi fotosensibili dei fotodiodi. In questo caso, il segnale ottico viene tradotto in un pacchetto di cariche fotogenerate che devono rimanere accumulate sulla capacità intrinseca del fotodiodo stesso fino al momento della lettura. E' dunque necessario che ad ogni pixel sia abbinato un elemento di indirizzamento, tipicamente un transistor, che garantisca accesso controllato e selettivo al fotodiodo corrispondente (matrice attiva). Al di là del fatto che in questo caso l'informazione ha una natura transitoria e la lettura risulta essere un'operazione distruttiva, nel caso di una realizzazione basata su elettronica stampata emergono anche altri svantaggi, quali: i) l'integrazione di dispositive diversi (un fotodiodo e un transistor) con tecniche di stampa non è banale; ii) la risoluzione spaziale dei dispositivi stampati è limitata, il che significa che il transitor occuperà una porzione significativa dell'area del pixel, a scapito del fill-factor.

In questa tesi proponiamo dunque un diverso approccio al problema, sviluppando pixels basati su una variazione fotoindotta di conducibilità in strati di biossido di titanio (TiO_2). L'idea di fondo è: se l'informazione ottica fosse tradotta in una variazione stabile di una proprietà elettrica del materiale attivo, piuttosto che in un

accumulo transitorio di carica, sarebbe possibile evitare l'utilizzo del transistor di indirizzamento. A questo scopo si è sfruttato un fenomeno noto per l'ossido di titanio, che consiste in un n-doping del semiconduttore legato all'espulsione fotoindotto di atomi di ossigeno dalla superficie del materiale stesso. Questo a sua volta si traduce in una variazione di conducibilità del materiale, la quale porta con sè tutte le informazioni necessarie riguardo al segnale ottico incidenete.

In questo lavoro di tesi, dopo aver introdotto brevemente il contesto in cui si inquadra l'attività (Capitolo 1), discuteremo in dettaglio la tecnologia proposta (Capitolo 2) in termini di principio di funzionamento, fabbricazione dei pixel e stato dell'arte.

Nel Capitolo 3 mostreremo che con tali pixel utilizzati in atmosfera inerte si può ottenere un range di variazione fotoindotta di conducibilità di più di tre ordini di grandezza. Dimostreremo inoltre che a valle della stimolazione ottica, si può ottenere un buon controllo sul processo spontaneo di ritorno della conducibilità al livello iniziale attraverso ingegnerizzazione del processo di fabbricazione, in particolare applicando o meno un trattamento di passivazione alla superficie dell'ossido dopo la deposizione.

Lavori precedenti hanno mostrato come questo tipo di pixel può funzionare correttamente se utilizzati in condizioni di alto vuoto, dove gli atomi di ossigeno espulsi a valle dell'illuminazione non possono essere facilmente reintegrate dal materiale e ci si aspetta che l'effetto di fotodoping sia permanente. Nel Capitolo 4 mostreremo che tali pixel in realtà possono funzionare correttamente anche in atmosfere diverse dall'alto vuoto, purchè la quantità di ossigeno e umidità presente sia trascurabile. Questo rappresenta un passo fondamentale dal punto di vista tecnologico. Infine, dimostreremo che i pixel in questione possono essere riutilizzati per più volte, indipendentemente dall'atmosfera in cui si sta lavorando.

Infine, nel Capitolo 5 riassumeremo i principali risultati sperimentali e trarremo le conclusioni.

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Chapter 1. Digital Imager and Conductance change pixels

For more than half a century, the main material of the electronics industry and optoelectronics has been silicon. The specialization of technical production linked to this material made the products in the electronics industry more and more pervasive in daily life. However, due to economic limitation, electronic devices based on alternative materials have come to be more popular in recent years. Such as organic semiconductors and metal oxides nanostructures. Most of these materials are processed from solution and using techniques similar to common printing techniques (such as inkjet or roll- to-roll), they open up the fascinating prospect of electronics at low cost, easily adaptable to applications with large area and compatible with the use of substrates of different nature, including plastic substrates and light flexible.

The use of new semiconductors materials can be varied, you can find them already in the production of OLEDs, transistors and photo detectors. They can indeed find profitable exploitation especially in those application fields where large areas are inherently required, like it is the case of medical imaging, since X-rays used for radiography cannot conveniently be focused onto smaller areas.

We propose indeed the use of a solution processable semiconductor, i.e. titanium dioxide, to target the development of large area panels for digital imaging. The core of a panel for digital imaging is a matrix of suitably designed photosensitive pixels, and the core of each pixel is in its turn the photosensitive element. Most commonly, the photosensitive element is a photodiode. We propose an alternative approach where the photosensitive element is given by a device whose electrical conductivity is changed by interaction with light.

1.1 Photodiode based pixel

In the standard approach, photodiodes are used as the photosensitive element. Upon illumination, charges are photogenerated inside the photodiodes. When a large number of photodiodes (pixels) have to be handled, such photogenerated charge in each one of them cannot be extracted and read in real time by the readout electronics, simply because this would imply to have a dedicated readout electronics for each pixel. Therefore, in this kind of systems， an addressing element, typically a transistor, must be present next to each detector. [1] [2] [3] The transistors of the array are all in the OFF position during the exposure to the radiation light: the photo charge generated from each photo detector is integrated on its parasitic capacitance to avoid crosstalk with adjacent devices. The transistors remain in OFF up to the reading phase, guaranteeing the preservation of information. During reading phase, the read out line accesses selectively the pixels of the ith row, and the corresponding transistors are switched ON (see figure 1).
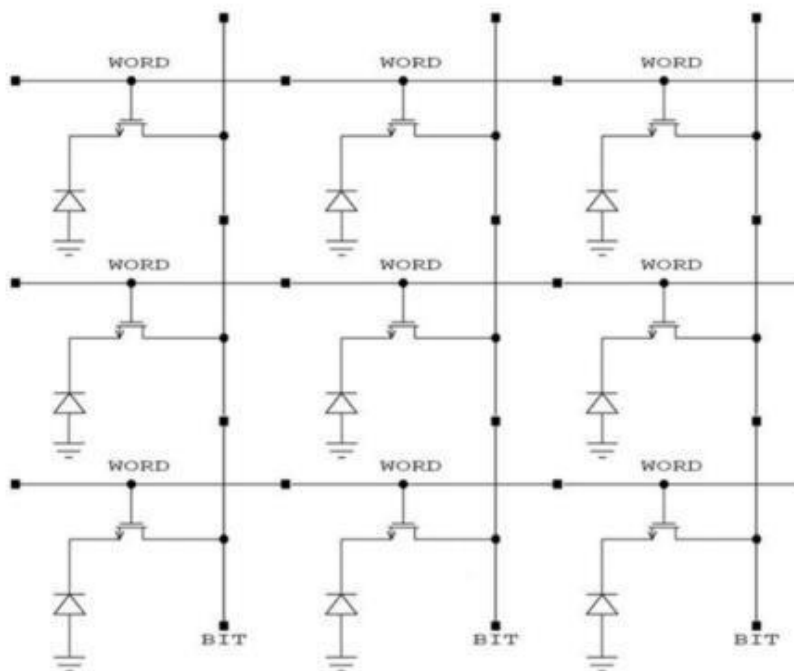
Figure 1 Active matrix of pixels, comprising photodiodes driven by transistors that perform the function both of isolation of the single photosensitive cell and reset of the photodiode. [5]

As showed, each pixel contains a photodetector and a transistor and it is prone to two major problems:

1) It is complex in terms of realization: integration of two elements by solution process technology is non-trivial;

2) The fill-factor of the single pixel is affected by the presence of the transistor. Because of the presence of the transistor, the actual area used to detect the incident light is only a part of the total area of the pixel. That is the reason why it is not always possible to achieve small pixel dimensions, especially if you work with solution processed semiconductors materials.

Therefore, the photodiodes based matrix has the following drawbacks:

➢ Transitory information

➢ Destructive reading

➢ Complex pixel structure

➢ Low fill-factor

Instead of being stored in the form of an accumulation of photogenerated charge dynamically, it would be different if the information concerning the irradiation of the pixel could be contained in a permanent and stable variation of an electrical property of the pixels, i.e. the conductivity in the case we propose.

1.2 Pixels Matrix Based on a Change of Conductivity

As reported in the literature, metal oxides have interesting qualities for the realization of optical detectors conductivity variation [4]. In particular, the titanium dioxide reacts easily with the ultraviolet radiation changing its electrical properties.
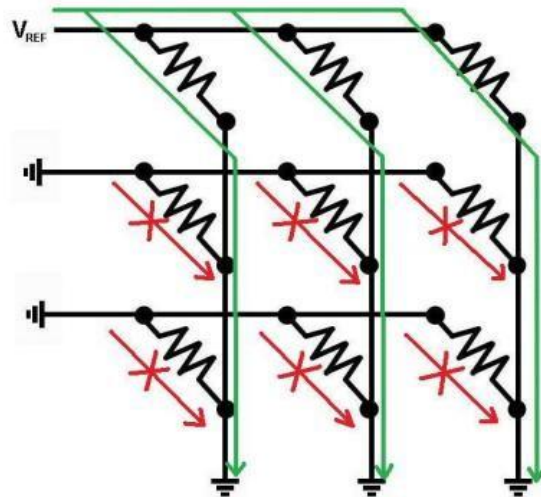
Figure 2. Resistive pixels matrix. Note how the conductive paths parasites do not interfere with the reading of the current loops through the pixels of the line analyzed since they are shorted to mass. [5]

In this case (see figure 2) the reading has the advantage of being ideally selective already at the time when a potential difference is applied between two electrodes of the row and column.

In fact, such a reading exclusively follows the Ohm's law. Current can pass only through the resistors subjected to voltage drop. In the other resistors no current flow is allowed. In this way, you avoid the undesirable effects of crosstalk easily without the need of the addressing element (the transistor). The information reading is thus performed by measuring the current passing through each pixel subjected to known voltage.

Therefore, in this way, using pixels matrix based on a change of conductivity we have the following advantages:

- Stable information
- Non-destructive reading
- Simplified pixel structure
- Maximized fill-factor

Chapter 2. Pixels based on photo-induced conductance change in titanium dioxide

2.1 Working principle
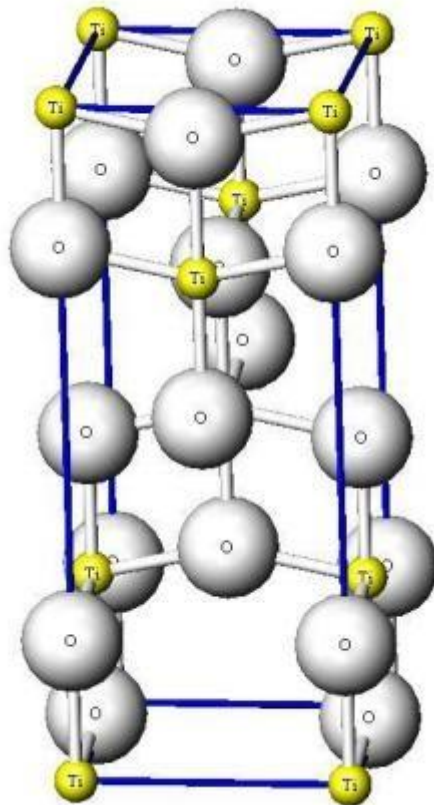
Figure 3 Conformation of crystalline TiO2 in the anatase form

As reported in the literature, TiO2 semiconductor shows strong reactivity when exposed to UV-light, this being a major problem for solar cells that exploit this material. [4] The physical mechanism behind this process is well-known: when a photon is absorbed by TiO2, which is only sensitive in the UV-region having a band gap of about 3.2 eV, a reaction is promoted by the photo-generated hole-electron couple that eventually results in the expulsion of oxygen atoms from the **surface** of the material.

By the formation of oxygen vacancies, free electrons are made available resulting in *n-doping* of the material, whose electrical conductivity is increased (*photodoping*). [6] [7] If oxygen vacancies are not replaced, i.e. if the material is kept in oxygen and moisture free atmosphere, this conductivity change is supposed to be stable. Successive exposure of the material to ambient condition is expected to reverse the mechanism due to reintroduction of oxygen atoms or OH- groups to passivate the vacancies.

2.2 Device architecture

The device is based on a sandwich-like structure where the photoactive material is interposed between two electrodes. One of the electrodes must be transparent, so to allow the light to reach the semiconductor. The chosen morphology for the TiO2 layer is a mesoporous one (details on fabrication will be provided in the following), where the photodoping effect can be maximized owed to the large extention of semiconductor surface. Oxygen atoms expulsion upon illumination is indeed reported to be mainly a surface phenomenon.

Though not strictly necessary for the device correct operation, a buffer layer like a compact, dense TiO2 layer could be present as reported in previous works [10] to reduce the risk of device short circuiting. [9] In this thesis work, we avoid the use of this extra-layer, thus demonstrating once again that the pixel structure can be simplified without affecting its electrical behavior.

The device structure is sketched in figure 4.

A surface treatment can be applied to the mesoporous TiO2 layer in order to passivate chemical defects and dangling bonds. This passivation treatment has been found indeed to play a key role in the device performance, as it will be shown by the experimental results.
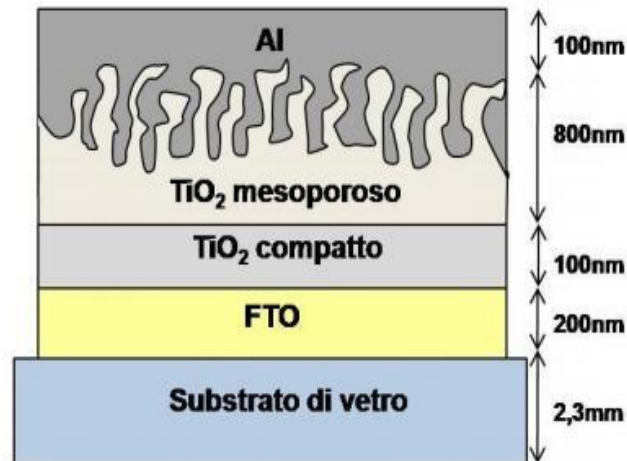
Figure 4 Structure of Vertical Devices based on TiO2. When present, the compact TiO2 buffer layer is interposed between the transparent bottom electrode and the mesoporous TiO2 layer.

As detailed in the following, the processes of deposition of TiO2 layers from solution need post deposition heat treatments at high temperatures (500°C). This entails the replacement of commonly used indium tin oxide (ITO) transparent electrode with the less conductive, rougher FTO (Fluorine opded tin oxide) (Figure 5), a similar with ITO, but capable of standing higher temperatures.
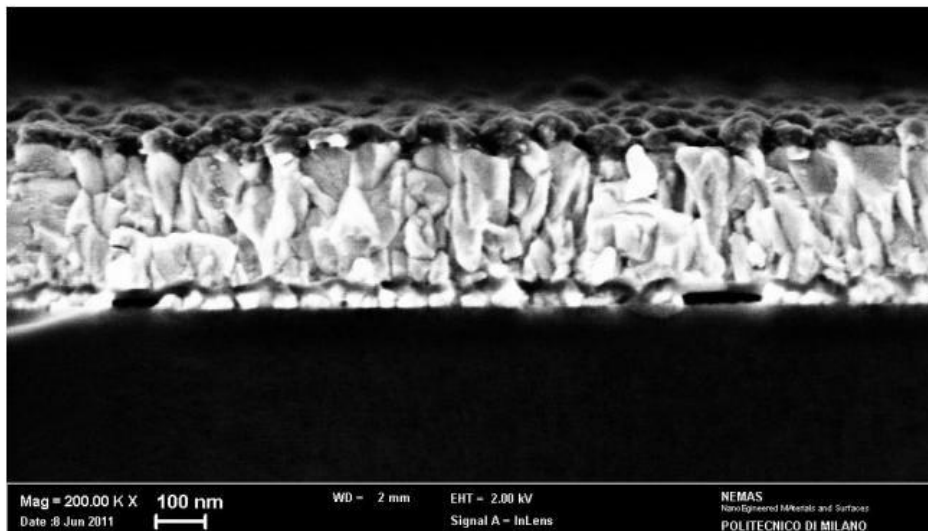
Figure 5   Scanning electron microscopy (SEM) image of a FTO layer (white) deposited on a glass base (dark, bottom). Above the FTO is deposited a thin film of TiO2 compact layer (upper dark layer). Note the considerable surface roughness of FTO. [5]

2.3 Device Fabrication

➢ Substrates preparation

Indium tin oxide (ITO) and fluorine doped tin oxide (FTO) are heavily-doped n-type semiconductors with a large band gap of around 4 eV. Due to the high energy gap, they are is mostly transparent in the visible part of the spectrum. In the ultraviolet, they are opaque because of band-to-band absorption (a UV photon can excite an electron from the valence band to the conduction band). In our case, FTO layer is used as the transparent electrode. Glass slides already provided with uniformely deposited FTO layer were bough from Pilkington ($\sim 15 \ \Omega \ \mathrm{per} \ \mathrm{sq}$).Then FTO layers were selectively etched (by masking with adeshive tape) with zinc powder and hydrochloric acid (2.4 M) in water solution to define the required pattern for the devices bottom electrode. Careful washing of the substrates following the etching step was performed with bidistilled water, acetone and isopropanol. Oxygen plasma treatment was finally performed for 5 minutes to remove the last traces of organic residues.

➢ Mesoporous TiO2 layer

A commercial Dyesol TiO2 nanoparticles paste (DSL 18NR-T), previously diluted in ethanol and ultrasonicated until complete mixing, was doctor bladed onto the substrate to get a mesoporous TiO2 film of an average thickness of 800 nm. The concentration of solution helps to determine the final thickness of the deposited layer. The substrates were then slowly heated to 500 °C (ramped over 1½ hours) and baked at this temperature for 30 minutes in air. Thickness of the layer was verified with a profilometer. [8] The high temperature post deposition treatment is required in order to get i) solvent evaporation; ii) burning of organic materials present inside the solution to provide solubility to TiO2 nanoparticles; iii) sintering of the nanoparticles.

➤ Surface treatment with TiCl4

When applied, the passivation treatment was done by soaking the substrates in TiCl4 solution (15 mM in water) and oven-baking for 1 hour at 70 °C. After oven-baking, the substrates were rinsed with bidistilled water, dried in air and baked again at 550 °C for 45 minutes.

➤ Aluminum top electrode

It is common to all samples: aluminum top electrode was thermally evaporated in high vacuum with suitable shadow masks (100 nm thickness).

In alternative, Ag is another material frequently used for electrode layer, which is costly in comparison.
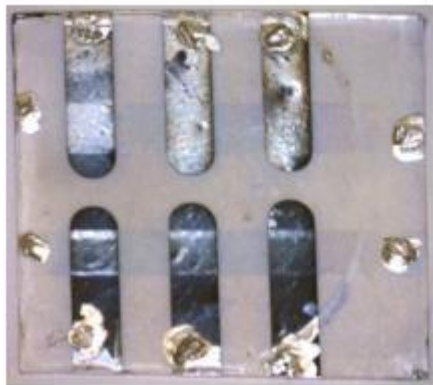
Figure 6 Prepared Device with Al on top

➤ Thermal annealing

All the devices were annealed for 1h in air at 80°C onto a hotplate right after aluminum evaporation. Based on the results proposed by G.M. Salvi in previous work, this step is required in order to remove possible traces of unwanted n-doping occurred during preparation. Thermal annealing in air is expected to promote the reincorporation of oxygens to passivate the vacancies.

Indeed, during thermal evaporation of the cathode, the TiO2 layer is exposed to light from an incandescent source (also containing UV), and it is in ultra high vacuum condition. Hence, it is reasonable to expect the TiO2 to be partially doped after this step.

2.4 State-of-the-art

Previous works [10] on such kind of pixels have shown that conductivity change of more than three orders of magnitude can be obtained upon UV light exposure, with current values ranging from hundreds of nA/mm2 (before illumination) to tens of mA/mm2 (saturation after few seconds illumination at 365 nm) for the devices biased at 1V. The devices had the structure described previously, comprising the presence of a buffer compact TiO2 layer to prevent possible device short-circuiting by direct contact between top and bottom electrode. Passivation treatment with TiCl4 was applied to the mesoporous layer. For the performed experiments, devices were kept in high vacuum environment (10^{-6} mbar) in order to prevent fast passivation of light induced oxygen vacancies by surrounding atoms present in air athmosphere (oxygen, moisture). For devices kept in high vacuum after illumination, the conductance jump upon UV light exposure showed a permanent and stable character over days of storage and monitoring. Recovery to the initial conductivity level could only be observed for devices exposed to air after illumination. A mild thermal treatment at 80°C eneabled the full recovery to be achieved within 1 hour.

Preliminary results were also reported [10], indicating a possible role played by the passivation treatment in determining the stability of conductance change phenomenon in high vacuum environment.

In this thesis work, we address two fundamental points of device behavior:

 1- We stress the role of TiCl4 passivation treatment in the stability of photodoping phenomenon by comparing the behavior of devices with and

without the treatment applied when stored in high vacuum environment after illumination (Chapter 3).

2- We explore the possibility of operating the devices in atmospheres different from high vacuum, aiming to demonstrate that less restrictive, more appealing (from a practical/technological point of view) working conditions can be envisioned for such objects. We explore in particular the following working atmospheres: high vacuum, mild vacuum, nitrogen, device encapsulation with epoxy resin (Chapter 4).

3. Reversibility check with and without TiCl4 treatment

In this chapter, we will address the spontaneous recovery behavior of TiO2 based pixel from the saturation conductivity value back to the initial "dark" value upon illumination. Previous works have shown the full reversibility can be obtained by exposing the chips in air after UV irradiation. We aim at engineering the chip so that full reversibility of the conductivity change effect can be obtained without the need for changing the working atmosphere of the chip. In prospect, this would simplified a lot the application from a technological point of view. In this chapter, we use in particular high vacuum environment for operating the chips, and we show that a significant role in the conductance recovery process is played by a passivation treatment that can be applied or not to the surface of the semiconductor.

3.1 Basic Measure Steps:

After chip preparation:

1. Cook the chip at 80 degree for 1 h in air condition.

   As a result of this treatment, passivation of oxygen vacancies possibly induced by fabrication process is expected. This step can be seen as a sort of chip "reset" made to ensure that the starting conductivity level before illumination (referred to as "dark" or "initial value") is the lowest possible for the chip (remove unintentional doping).

2. Leave the chip in vacuum, make sure the environment is dry and with few oxygen.

   Obviously, in vacuum it's considerably less probably that oxygen atoms expelled by absorption of a photon are replaced by other atoms present in the measurement environment. Thus, the conductivity change is expected to occur effectively and to be permanent. The vacuum chamber in CNST

electronic lab provides a low pressure environment under 10E-5 mbar with a pump working at 1500Hz.

3. Measure the chip in dark：

    To check the connections and the original conductance, it is necessary to measure the chip in dark. The result would be important reference of the change of conductance after UV light. "Forward" measurement is taken with the FTO contact kept at ground and the Al top contact at + 1V. "Reverse" measurement is taken with the FTO contact at ground and the Al top contact at – 1V.

4. Apply UV light.

    During our study, we use a lamp which provides 365nm UV light, correspond to 3.4 eV, a little bit higher than the energy gap (3.2 eV) of the material. The light intensity of UV irradiation is ~ 15 µW/mm2.
    To avoid the power of UV light damage the chip, it is better to apply the light gradually until it reaches saturation. 2 seconds per time for instance. Measure it immediately.

5. Leave in vacuum for several hours, up to one day, and measure again. Chips will be left in vacuum and dark situation for a period to check the stability of photo-induced conductance change phenomenon.

3.2 Measurements and results:

We compare the experimental results of tests made on chips provided or not with a TiCl4 based surface passivation treatment as described in Chapter 2.
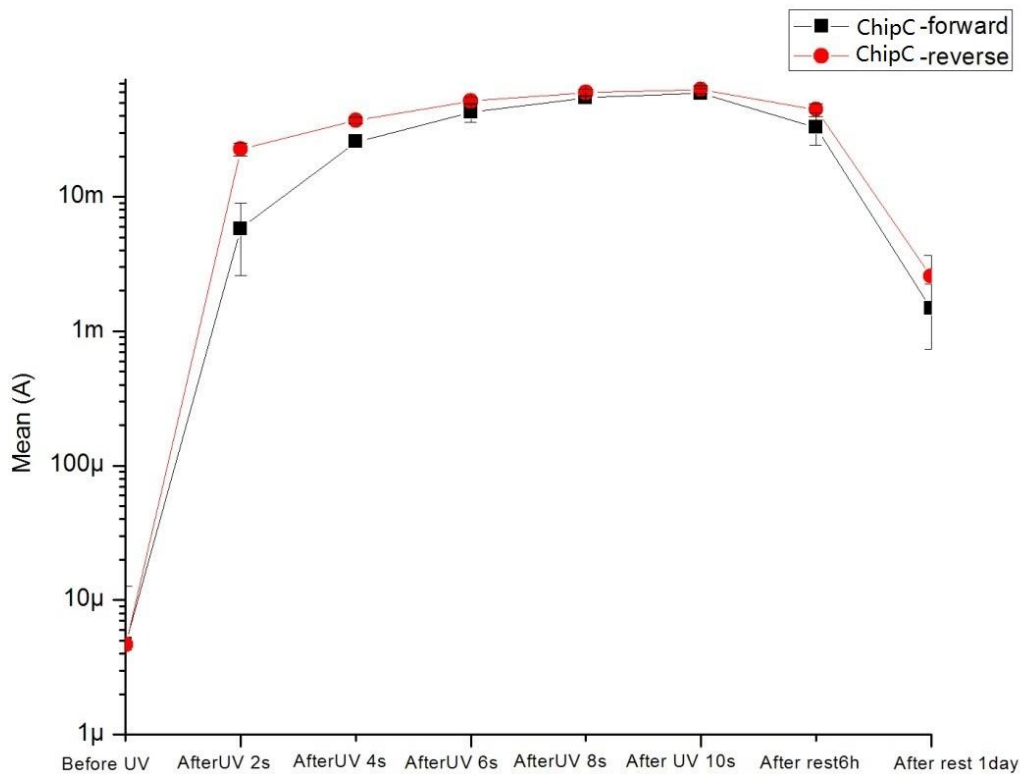
➢ **With Surface Treatment: chip C**

Figure 7 The mean current curve of Chip C （with surface treatment） before and after UV light. "Forward" measurement is taken with the FTO contact kept at ground and the Al top contact at + 1V. "Reverse" measurement is taken with the FTO contact at ground and the Al top contact at – 1V.

The behavior of this chip is in good agreement with what already shown in previous works:

1. From initial conductivity values around 5uA, saturation is reached at ~30-40 mA in few seconds of UV light exposure.

2. With the chip kept in high vacuum environment after illumination, the conductivity only decreases slightly over time. After 24 hours, the current still

remains at a very high level compared to the initial one, thus showing a poorly reversible behavior for this kind of chips.
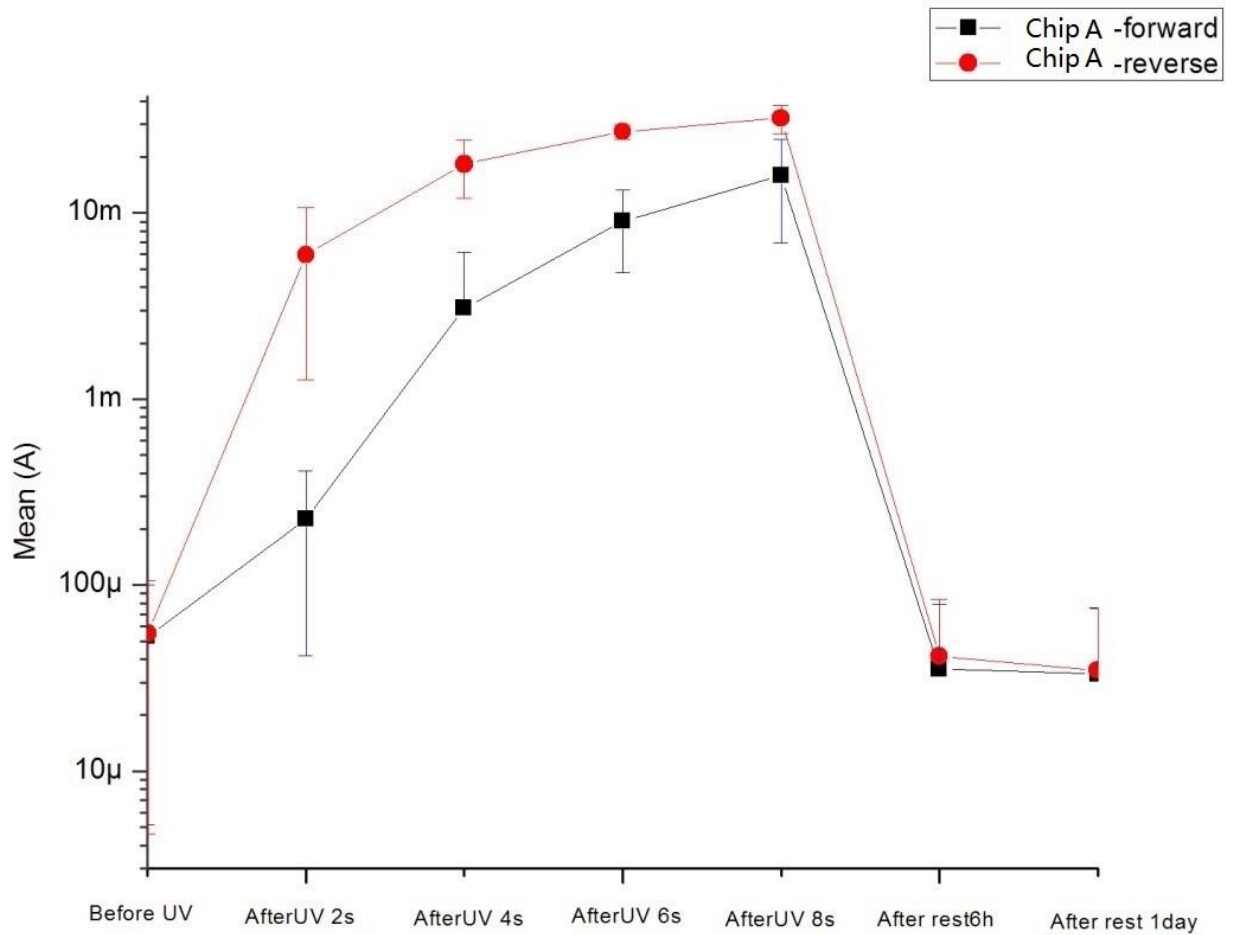
➢ **Without Surface Treatment: chip A and chip B**

Figure 8 The mean current curve of Chip A （without surface treatment） before and after UV light
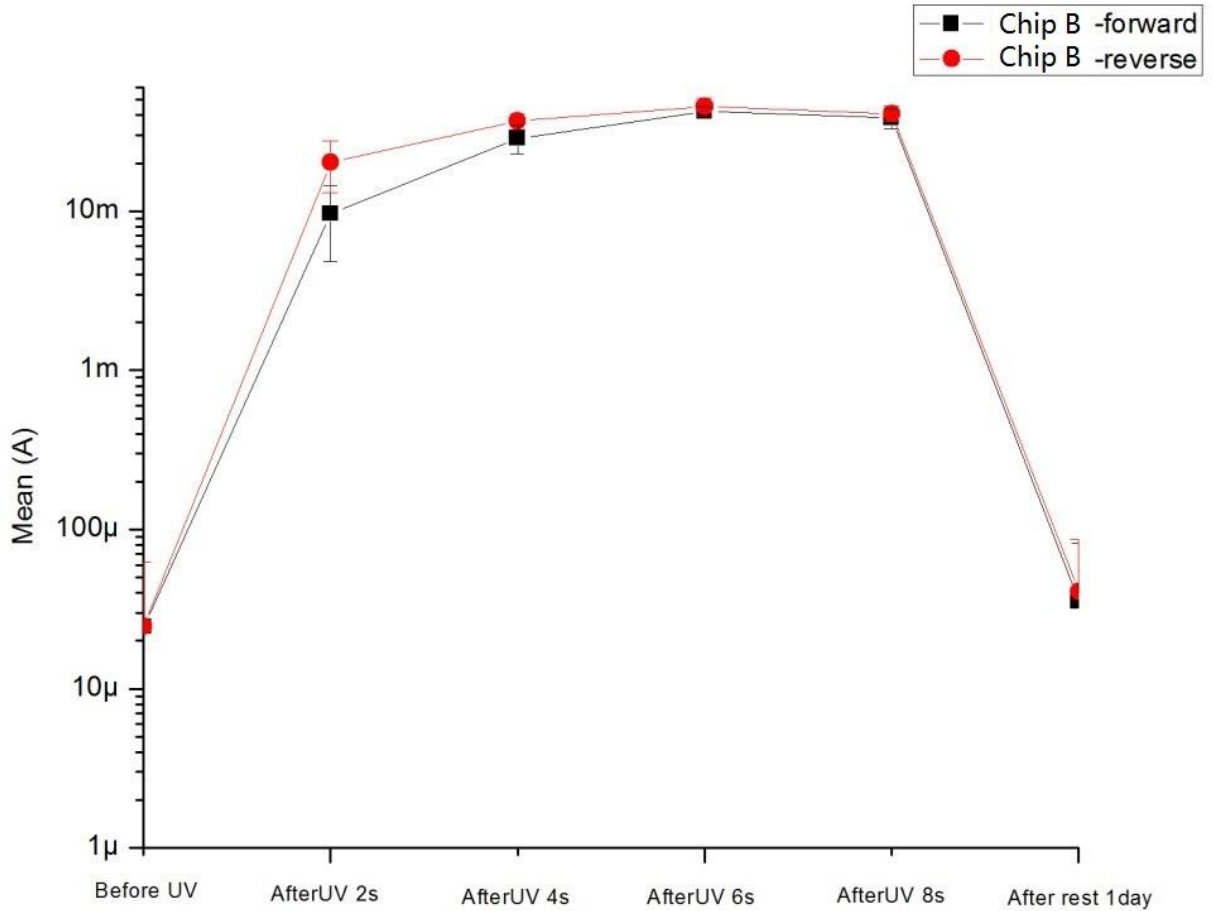
Figure 9 The mean current curve of Chip B（FTO without surface treatment）before and after UV light

1. We could clearly see that when we shine with the UV light, the current increases until reaches the saturation point, which are 20~30 mA, the same for both chips, although the initial value of chip A (50uA~60uA) is a little higher than chip B (20uA~30uA). This little difference could be attributed for instance to slightly different thickness or TiO2 layer.

2. For both chip A and chip B the conductivity level returns back to initial values within 24 hours after illumination, thus highlighting the strongly reversible behavior of chips when TiCl4 treatment is not applied.

3. From chip A we can also see that the current decreases very fast after rest in vacuum and in the later duration 6h to 1 day, it decreases slightly till finally reaching the initial value.

4. Forward and reverse measurements are always very similar, suggesting that the metal/semiconductor interfaces (FTO/TiO2 and TiO2/Al) for the devices under investigation behave in a symmetrical way.

➢ Conclusions

The tests performed on nominally identical chips, only different for the presence or not of a surface passivation of mesoporous TiO2, clearly show that the chip behavior gets stabilized by the application of the passivation treatment. Upon illumination, the presence of the surface treatment guarantees that the conductivity level is preserved for long time if the chip is kept in inert environment. On the opposite, spontaneous recovery in the same conditions can be achieved on a much faster time scale in the case of chips without the treatment applied. Investigation of the physics behind this behavior hasn't been addressed by this thesis work and will be subject of future work.

4. Test in different working conditions

We know from the literature that the photo-doping phenomenon exploited here to get light-induced conductance change is related with oxygen atoms expulsion from the material upon interaction with photo-generated carriers. Photo-induced oxygen vacancies cannot be promptly passivated by other atoms if the devices are kept in an inert, oxygen/moisture free environment.

For this reason, previous works have exploited high vacuum environment to get sizable and stable conductivity change in TiO2 based devices. However, high vacuum is far from ideal working condition from a technological point of view, as it requires complicated and expensive instrumentation. For this reason, here we tested the behavior of TiO2 based devices in atmospheres different from high vacuum, namely

1. In Air

2. In High Vacuum

3. In Rough Vacuum (a mild vacuum level: some air is inside)

4. In Nitrogen (operated in glove box)

5. Encapsulated (encapsulation with epoxy resin), aiming at finding more favorable conditions where to operate our pixels in a satisfactory way.

4.1 Basic Measure Steps

After device preparation:

1. Cook the device at 80 degree for 1 h in air condition. As described in Chapter 3.

2. Leave the device in the desired atmosphere for at least half an hour:

    1) in Air

    2) in Vacuum (with the pressure 10E-5 mbar with turbomolecular pump on working at 1500Hz)

3) in Rough Vacuum (near the pressure 1.2 mbar without turbomolecular pump on)

4) in Glove Box (in the atmosphere of Nitrogen, and inside a glove box typically oxygen and water levels are below 0.1 ppm (part per million)

5) in Encapsulated condition (encapsulation with epoxy resin)

3.   Measure the device in dark.

4.   Apply a short UV light for 16s to make sure that the device reached the saturation level. During our study, we use the same UV lamp as described in Chapter3. Then measure it immediately.

5.   Leave the device in different conditions for an hour after illumination, and then measure them again.

6.   Leave the devices in the particular conditions for one day after illumination. And measure them again. Devices will be left in different situation for a period to check the stability.

7.   And test in the same procedure for multi cycles in Vacuum and Encapsulated condition to check on reusability of the pixel.

4.2 Measurements results

4.2.1 Compare the conditions (Air/High Vacuum/Rough Vacuum)

Firstly we consider the first three conditions (Air/High Vacuum/Rough Vacuum). After testing different groups of nominally identical chips, we have the following founds:

➢ **Group 1 and Group 2**

For each device, after testing and recording all the data (currents in A), we divide by the active area thus getting the current per unit area (A/mm2).
And then we take the average value of all the pixels on each chip, we have the following graph:
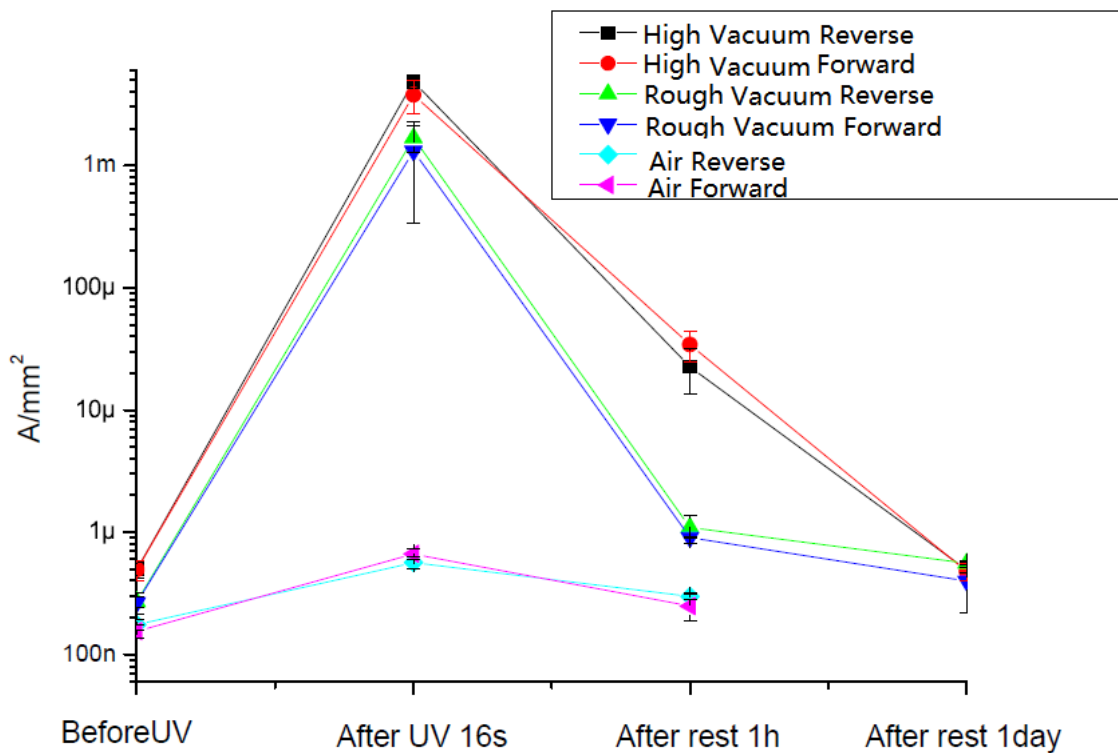

Figure 10 Group 1 tested in Air/High Vacuum/Rough Vacuum conditions before and after UV light
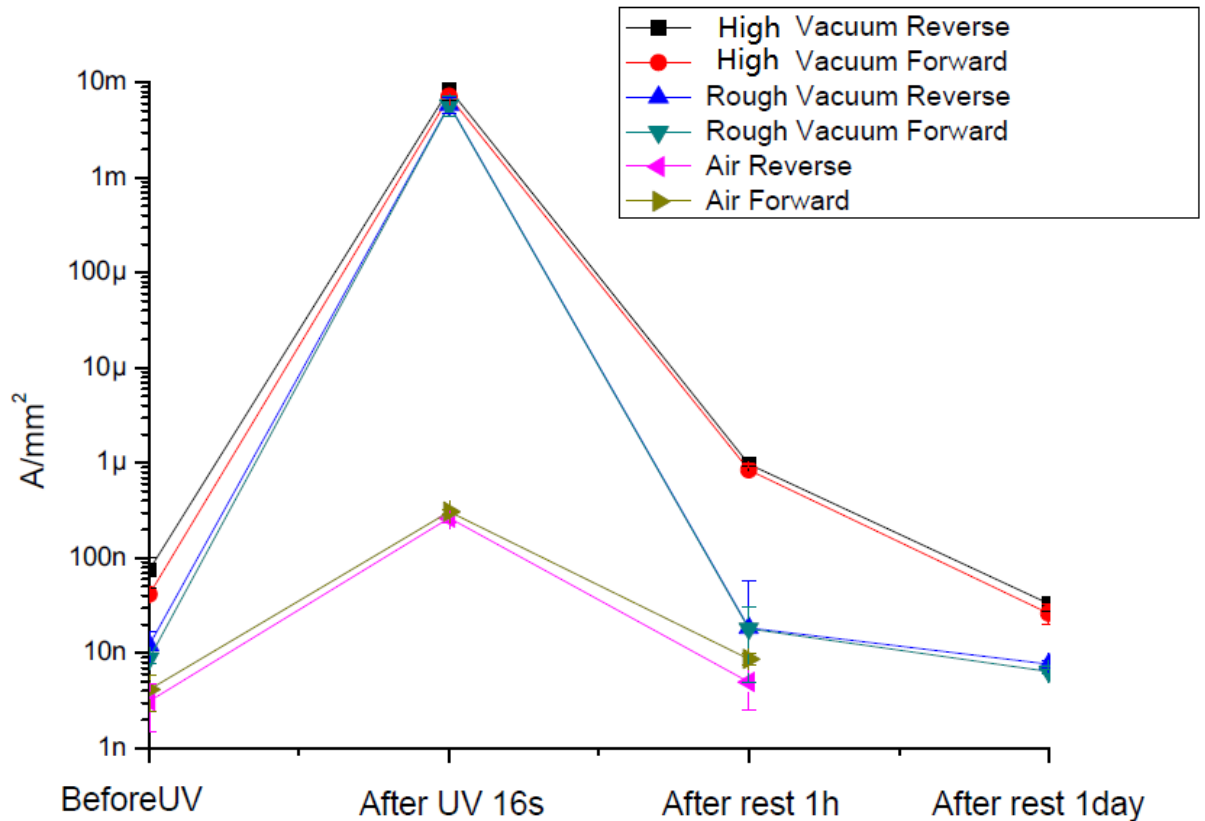
Figure 11 Group 2 tested in Air/High Vacuum/Rough Vacuum conditions before and after UV light

As we can see from the two graphs, the initial and saturation conductivity of the two groups are slightly different, and maybe this is caused by TiO2 layer thickness variation during the fabrication. Also the group 2 has a higher photo-response in air. However, the trends of the two groups and the dynamic behavior are very similar, and we could easily get that:

1. Both three cases show a nice reversible behavior, after 1 day they all tend to recover to the conductivity level before the UV light.

2. High Vacuum and Rough Vacuum compare:
    In the rough vacuum condition, both initial conductivity and the conductivity after UV light are slightly smaller than the conductivity in High Vacuum, more or less the half of the High Vacuum value.

3. In Air condition:
    After UV light, the saturation value is much smaller than the previous two cases, almost as a factor of 1000, and it recovers very fast to the initial value, in 1 hour. The change in air is almost negligible.

To summarize:

✓ The conductivity level in three cases:

Conductivity level in Air < in Rough Vacuum< in High Vacuum, which is also reasonable because the amount of air in three cases is decreasing one by one.

✓ The initial conductivity level doesn't show huge difference in different conditions, while the conductivity after saturation has a big change:

✧ Rough Vacuum is almost half of the High Vacuum value.

✧ Air condition is almost 1/1000 of the High Vacuum value.

This can be likely attributed to an initial intrinsic doping of the TiO_2 material, depending on the presence of air and in particular increasing in the absence of air.

✓ The recovery time of Rough Vacuum condition is much faster than the High Vacuum condition. This, again, can be easily traced back to the higher amount of oxygen and moisture present in the rough vacuum environment compared to the high vacuum and responsible for passiovation of photoinduced oxygen vacancies.

4.2.2 Compare the conditions High Vacuum/Rough Vacuum/Nitrogen for group 2

Then we take the devices of group 2 and we repeat the experiment, but all inside a Glove Box, where pure nitrogen atmosphere is present. And we get:
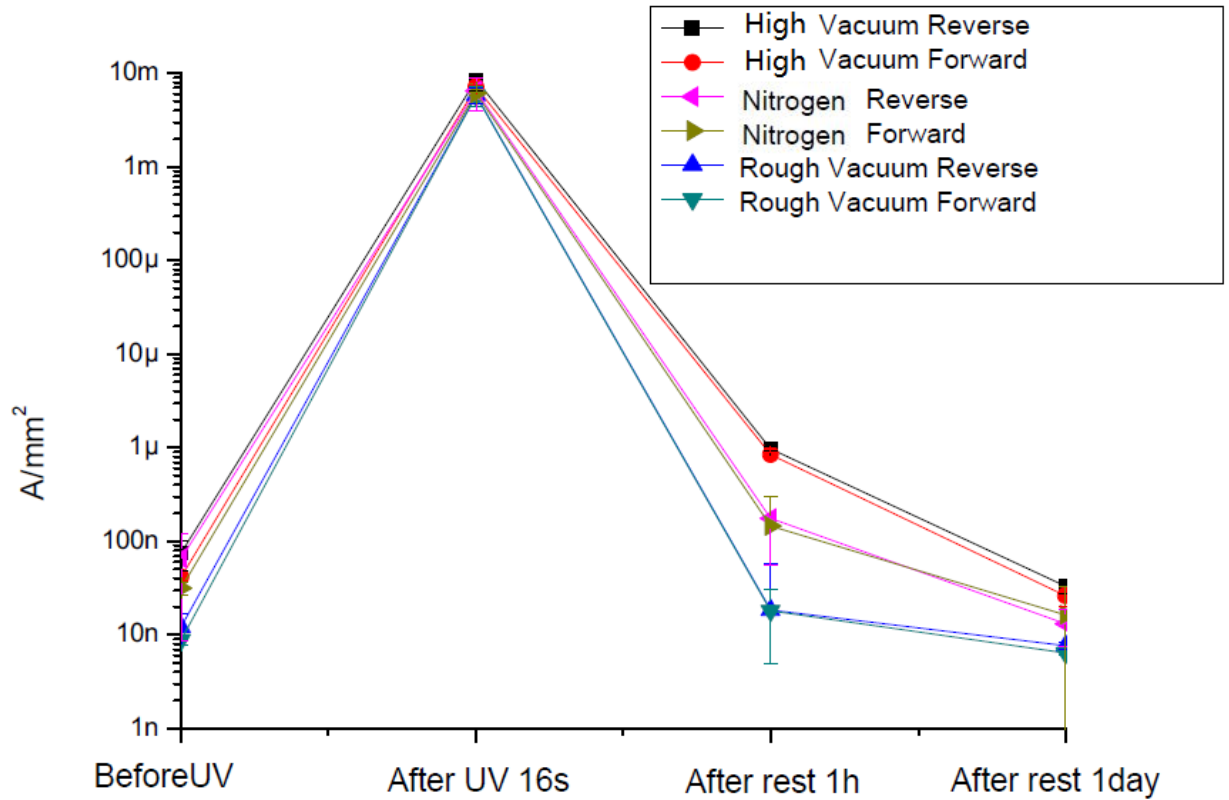
Figure 12 Current per area of devices in Group 2 tested in Nitrogen/Vacuum/Rough Vacuum
    conditions before and after UV light

From the graph, we could conclude that:

1. The initial value of the Nitrogen condition and High Vacuum condition is almost
   the same, Nitrogen condition is just slightly smaller than the High Vacuum level.
   And both of them are bigger than the rough vacuum condition, as a factor of
   10.

2. The saturation values of both three cases are more or less the same.

3. The recovery speed of the three cases:
   In High Vacuum < In Nitrogen< In Rough Vacuum, suggesting that the
   presence of air inside the glove box could be something in-between the
   rough vacuum and the high vacuum level.

To summarize:

✓   the conductivity level in three cases:
Conductivity level in Rough Vacuum < in Nitrogen < in High Vacuum,
and the behavior of the Nitrogen condition is between the rough
vacuum condition and High Vacuum condition.

4.2.3 Compare the conditions: Air/High Vacuum/Rough Vacuum/Nitrogen/encupsulated

Then we take the one of the chips in group 2 (chip 7) and we encapsulate it with
epoxy resin, so that air is not allowed to reach the devices. Encapsulation is done
inside the glove box. Then, we directly test the chip in air and make the same
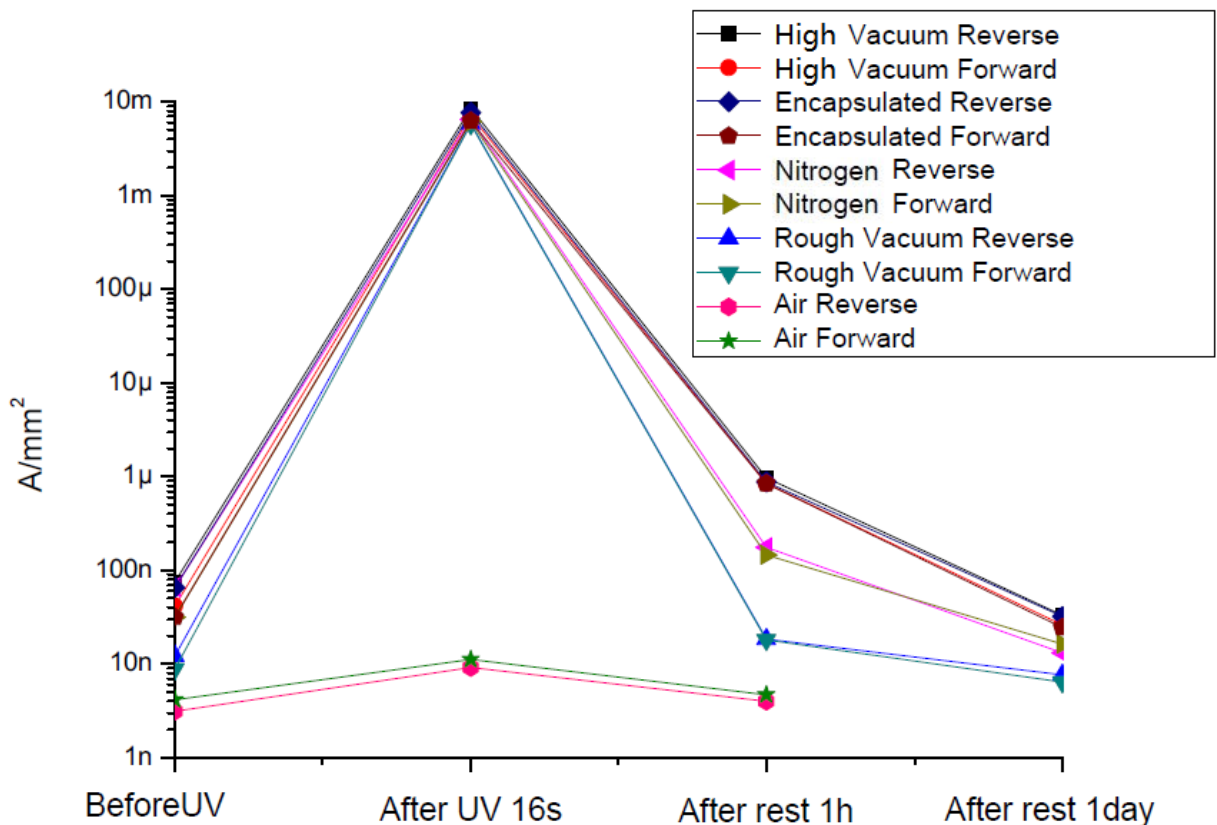measurements again, we get:

Figure 13 Current per area of chip 7 tested in Air/High Vacuum/Rough
Vacuum/Encapsulated/Nitrogen conditions before and after UV light

From the graph, we could clearly see that:

1. The behavior of the encapsulated devices and devices kept in high vacuum condition is almost the same, both for the initial value and saturation value, together with the recovery speed. This is suggesting a very negligible amount of air is present inside the chip upon encapsulation.

2. Conductivity level in Air < in Rough Vacuum< in Nitrogen< Encapsulated≈ in High Vacuum, likely because the amount of air around is decreasing one by one.

3. All of the conditions above work very well except in Air, where the change after UV light is almost negligible.

4.2.4 Check the re-usability of the devices

Finally, we want to check the re-usability of the devices by performing multiple cycles of writing (UV exposure) and erasing (device at rest for a given amount of time). We compare in particular the operation of the devices in high vacuum condition with the encapsulated devices. In the case of devices stored in high vacuum, good repetibility is expected. In the case of the encapsulated devices, the high chemical reactivity (known in the literature) of photoexposed TiO2 could in principle get to some unwanted interaction between the semiconductor itself and the epoxy resin, possibly compromising the re-usability of the devices. For device in high vacuum, we get the following result:
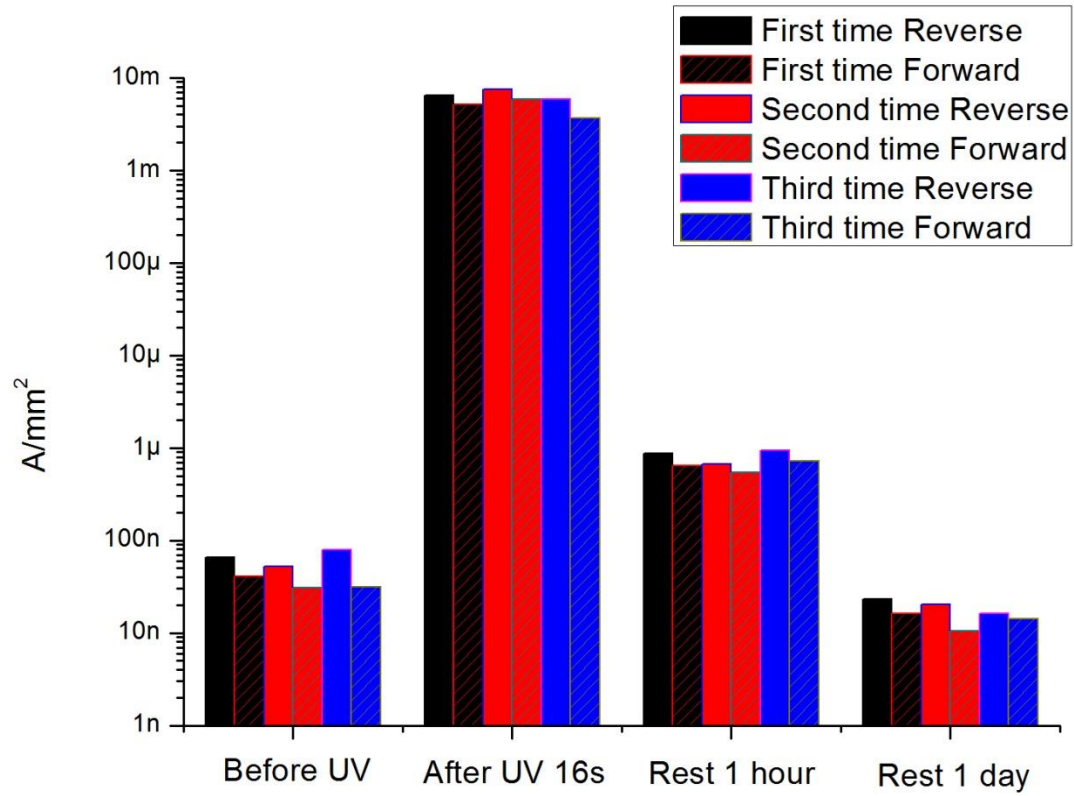
Figure 14 Current per area of device 4 tested in Vacuum condition in different cycles and times

From the graph above, we could clearly see that:

The behavior of all the three measure times is almost the same, which indicates that the device is reusable for many times.

For the encapsulated devices, we get the following result:

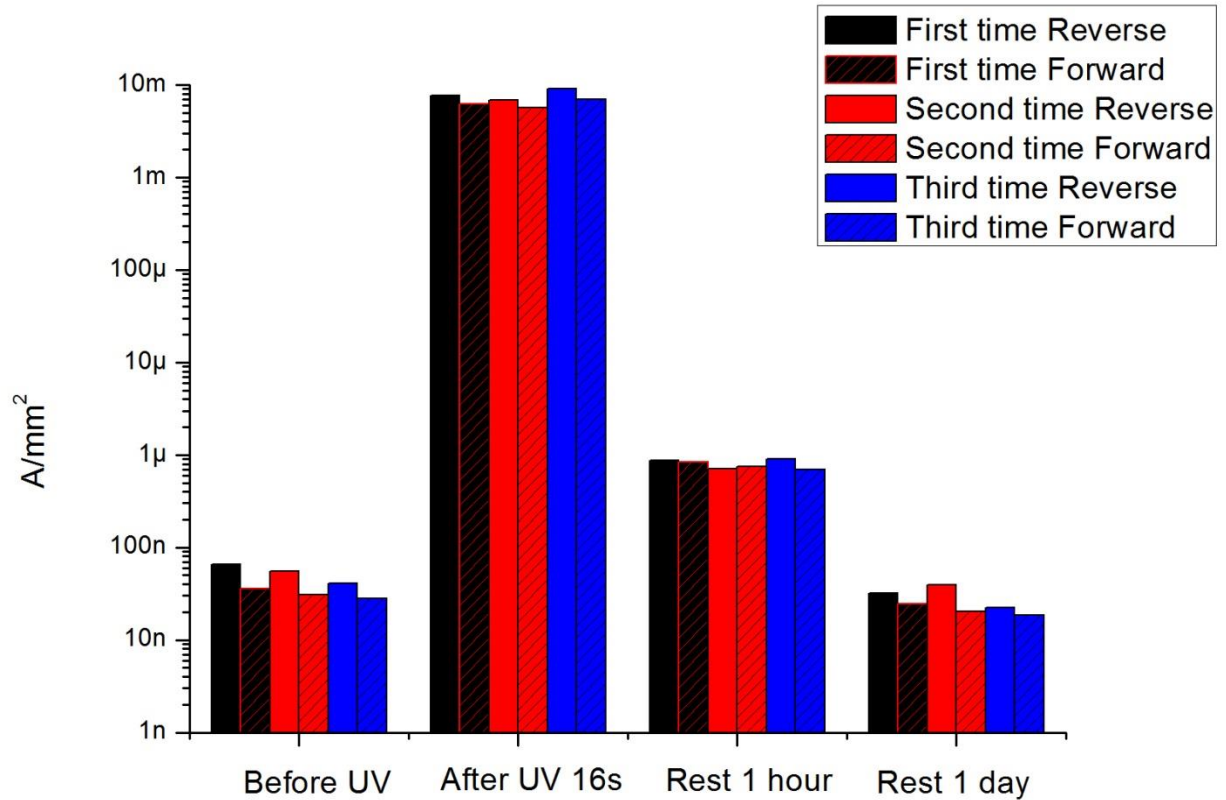Figure 15 Current per area of device 7 tested in Encapsulated condition in different cycles and times

From the graph above, we could clearly see that the behavior of all the three measure times is almost the same, which indicates that the device is reusable for many times. This is suggesting that no chemical reaction occurs between the photo-stimulated TiO_2 and the epoxy resin used for encapsulation.

5.Conclusions

We focused our research activity on developing photosensitive devices based on light induced conductance change in titanium dioxide. Such kind of devices can be used as pixels in a matrix configuration to target imaging applications. Owed to the light information being translated into a stable change of the active material electrical properties and to the reading operation being not destructive, here the presence of an addressing element for each pixel, typically required in photodiodes based matrixes, can be avoided.

The photodoping phenomenon that we exploit is related with oxygen atoms expulsion from the semiconductor surface upon photogeneration of charges. By deeply characterizing the devices behavior, we showed that operating the devices in an atmosphere free of oxygen and moisture is necessary condition in order to see sizable conductance change. Otherwise, photoinduced oxygen vacancies are promptly passivated and the photodoping effect is lost.

While in an oxygen/moisture free environment the conductance change is expected to be indefinetly stable, indeed we show that reversibility of the phenomenon can be controlled to a certain extent by playing with surface passivation of the semiconductor. More specifically, for devices kept in oxygen/moisture free environment after illumination, we show that long time standing photodoping effect is obtained only if a passivation treatment with titanium tetrachloride is applied to the surface of TiO2. Otherwise, full reversibility of the effect is achievable within few hours.

By comparing different possible working atmospheres, namely high vacuum, mild vacuum, nitrogen and air, we could indeed verify that the amout of residual oxygen/moisture in the ambient of operation controls the behaviour of the devices.

In particular, the speed of device return to the initial conductivity state upon illumination turns out to be strongly dependent on this parameter, the return being faster in mild vacuum than in nitrogen, in nitrogen than in high vacuum. In air, negligible change of the conductance can be appreciated compared to the other cases.

However, we demonstrated that correct operation of the devices in air environment can be made possible by providing them with suitable encapsulation made of a

commercial epoxy resin. The performances of encapsulated pixels measured in air turned out to be totally comparable in terms of conductivity values, conductivity change upon illumination, recovery time and rewritability, to those of pixels measured in high vacuum environment. This represent a key finding, as it enables correct operation of the devices regardless the environmental conditions in which the actual measurement needs to take place.

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