Development of Imaging Pixels Based on UV-light Induced Conductance Switching in Titanium Dioxide

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Abstract I

With the wide application of digital imaging technology, the traditional silicon technology is ill-suited in many fields because of the high requirement on manufacture and cost as the detecting areas increase in size. Researchers are trying to exploring new kinds of semiconductors that can be solution processed in a cost-effective way by means of techniques amenable to large area covering.

In this thesis work pixels based on such new technology have been developed, having solution processed titanium dioxide (TiO2) as photosensitive material. The pixel working mechanism is based on the stable change of active material conductance upon irradiation with UV light. In conventional photodiode based pixels, the light information is store dynamically in the form of photogenerated charge accumulated on a capacitance. This implies that each pixel must be kept isolated until the time of reading by a suitable addressing element, i.e. a transistor. On the opposite, the non-transitory nature of the information in our case allows the pixel structure to be significantly simplified, as addressing elements in addition to the photosensitive one are not required.

In this thesis work, the electrical behavior of TiO2 based pixels is explored in depth and correlated with different processing protocols and device structures. Conductivity change of more than 3 orders of magnitude has been shown upon UV light exposure. Reversibility of the mechanism has been also demonstrated, together with the possibility of lowering the device processing temperature down to a value (200 C) compatible with pixel realization onto cheap, flexible and light weight plastic substrates.

Abstract II

Le applicazioni che prevedono l'utilizzo di pannelli digitali per imaging sono al giorno d'oggi molteplici. A questo scopo e in particolare quando l'applicazione prevede un'ampia area fotosensibile, la tecnologia tradizionale basata su silicio mal si adatta a causa della complessita' e degli elevati costi di produzione.

Per questo attuale focus di molti gruppi di ricerca e' lo sviluppo e l'utilizzo di nuovi materiali semiconduttori che si possano lavorare da soluzione con tecniche a basso cost e scalabili su ampie superfici.

In questo lavoro di tesi sono stati sviluppati pixel basati su questa nuova tecnologia e aventi biossido di titanio (TiO2) lavorato da fase liquida come materiale fotoattivo. Il principio di funzionamento del pixel proposto si basa su una variazione stabile di conducibilita' dello stesso a valle dell'irraggiamento con luce UV. In pixel di tipo piu' tradizionale basati su fotodiodi, l'informazione luminosa e' tradotta dinamicamente in carica elettrica che viene accumulata su una capacita'. Questo implica che ciascun pixel deve essere mantenuto isolato dagli altri fino al momento della lettura attraverso un opportuno elemento di indirizzamento, ad esempio un transistor. Al contrario, la natura stabile e non transitoria dell'informazione nel caso del qui proposto rende superfluo il ruolo dell'elemento di accesso, permettendo di semplificare la struttura del pixel in modo significativo.

In questo lavoro di tesi, il comportamento elettrico di pixel basati su TiO2 e' stato studiato a fondo e correlato a diversi possibili protocolli realizzativi e diverse strutture del layer fotoattivo. E' stato possibile dimostrare per i pixel in questione una variazione di conducibilita' di piu' di tre ordini di grandezza a valle di esposizione a luce UV. E' stato inoltre possibile provare la reversibilita' del fenomeno, oltre che la fattibilta' di realizzare i dispositivi attraverso ricette a bassa temperatura (200 C) compatibili con substrati plastici economici, leggeri e flessibili.

Introduction

Digital imaging technology is playing a significant role in various applications like digital radiography in biomedical field, industrial quality control, environmental monitoring, and homeland security. The traditional silicon technology is ill-suited for these purposes because of the high requirement on manufacture and cost of large area sensor. Researchers are trying to exploring new kinds of semiconductors for the application purpose, which may be deposited through techniques based on the classical techniques of graphic arts printing, and are therefore compatible with the covering of large areas.

However, this new technology is still limited by integration processes and materials. A standard pixel for imaging consists at least of two devices: the unit photosensitive (photodiode), and the addressing element (transistor). The integration of the photodiode and transistor requires different active materials (optimized respectively for the photo generation and transport), while preserving the pixels for a high fill factor at the same time. It presents significant difficulties in the current state of development of these emerging technologies.

The need to have an element in the pixel isolation and addressing is naturally result of the fact that the photodiode translates a stream of photons into a transitory information, i.e. a given amount of photogenerated electrical charge. In order for the information carried by each pixel to be preserved till the time of reading, isolation of each photodiode is required so that photogenerated charge is not shared and hence lost.

The transistor would not be necessary if instead the optical information would be translated into a stable variation of electrical parameter (for example the conductivity) of the photosensitive member. The possibility of realizing conductivity variation pixels have been demonstrated in a previous thesis work, which discussed a workable devices based on nano-structured titanium dioxide (TiO2). The proposed mechanism for change of pixel conductance is the UV-light induced n-doping of the semiconductor. Being mutuated for transitory reasons by the class of dye sensitized solar cells, the proposed device based on TiO2 semiconductor was in that case realized by high temperature processing and was characterized by a rather complex structure. This thesis is focused on further developing the concept of TiO2 based pixel, trying to investigate more deeply the working principle of the device as a tool to engineer its structure towards a simplified, low temperature processed version of what proposed in the previous work. The proposed pixel is selectively sensitive to UV-light, which might be premium feature for some fields of applications. As an example, this absorption range is well matched with the emission of many scintillating materials commonly used for the indirect conversion of X-ray photons. The activity was conducted at the Department of Electronics, Information and Bioengineering of the Politecnico di Milano, in close collaboration with the Center for NanoScience and Technology of the Italian Institute of Technology in Milan.

The paper is structured as follows. Chapter 1 provides a brief introduction to the theoretical work; Chapters 2 describes in detail the experimental development of pixel based on titanium oxide, state of the art devices and devices realized by varying the fabrication process and the overall composition of the semiconductor layer. Chapter 3 demonstrates the measuring steps and different measuring runs in different consideration. The result will be analyzed in Chapters4.

1. Matrix

For more than half a century, the main material of the electronics industry and optoelectronics is 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 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. The can indeed find profitable exploitation especially in those application fields where large area are inherently required, like it is the case of medical imaging, since X-rays used for radiography cannot conveniently be focused onto smaller areas.. If the array is made of silicon, it involved in an important issues both from the point of view of costs and the production process. Hence, thanks to the remarkable economic and technological advantages introduced by this type of materials, possible solution using alternative machinable materials is a huge benefit compared to the use of silicon.

The experimental work performed in this thesis: solution processable semiconductor (TiO2) is explored in order to realize photo resistive pixels, that is, the information is not stored in the form of charge, but in the form of permanent variation of the electrical conductivity. These may be the basis concept for the construction of a conductive pixels matrix for medical imaging. At the same time, a device with different structure is explored starting from experimental results highlithed in a previous thesis work proposed by G.M. Salvi.

1.1 Active matrix of pixels

In a matrix of optical sensors (pixels), a transistor is present next to each detector which acts as addressing device.[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 access selectively to the pixels of the ith row, and the transistors are brought into ON of the same row (see figure 1).

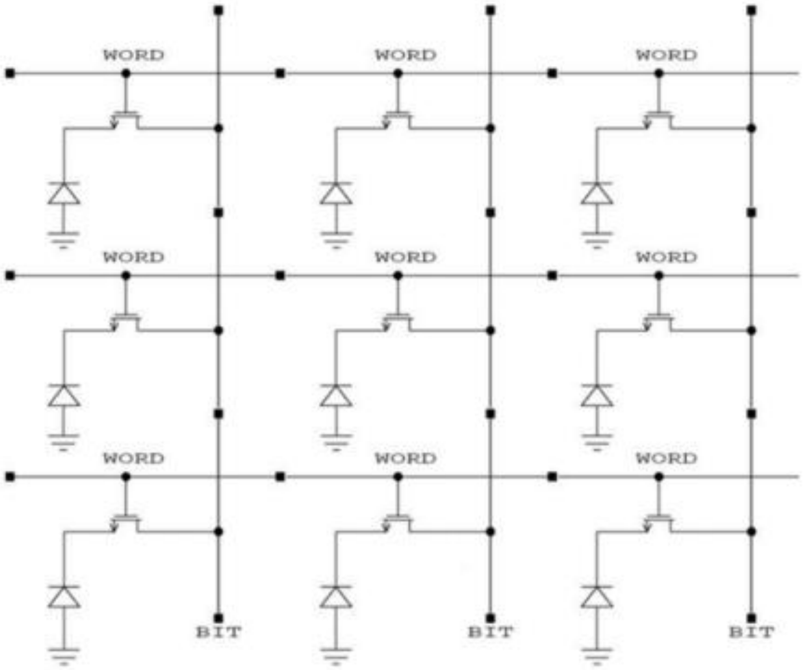

Figure 1 Active matrix of pixels, comprising photodiodes driven by transistors that perform the function both of isolation of the single photosensitive cell and reset of the photodiode.[5]

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

1) It is complex in terms of realization: intergation 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.

Instead of being stored in the form of an accumulation of photo generated 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

Given the advantages listed above, in this paper we have explored different ways for the realization of an array for imaging based on pixels showing stable conductance switching upon illumination.

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. The description of this phenomenon and devices made of TiO2 will be provided in following Chapter, where it will be also analyzed the implementation of a prototype array of TiO2 based pixels.

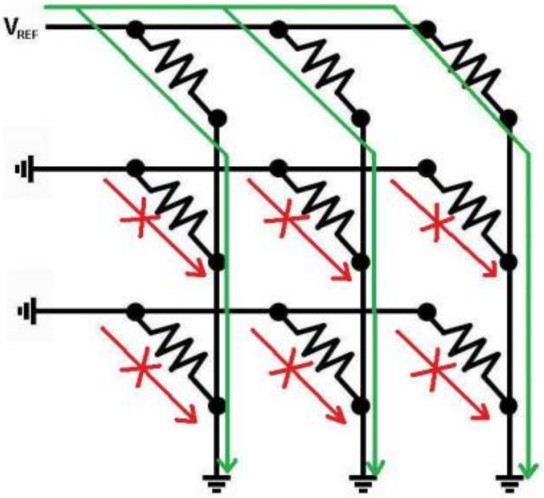

Figure 2. Resistive pixels matrix. Note how the conductive paths parasites do not interfere with the reading of the current loops through the pixels of the line analyzed since they are shorted to mass.[5]

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 affected by this potential difference subjected to voltage drop. Other resistors cannot pass any current that goes to be disruptive to the measure because nothing short circuited. In this way, you avoid the undesirable effects of crosstalk easily without the need of the address of a transistor. The information reading is thus performed by measuring the current passing through each pixel subjected to known voltage.

2. Vertical Devices Based on TiO2

2.1 TiO2 Material and Photodoping Mechanism

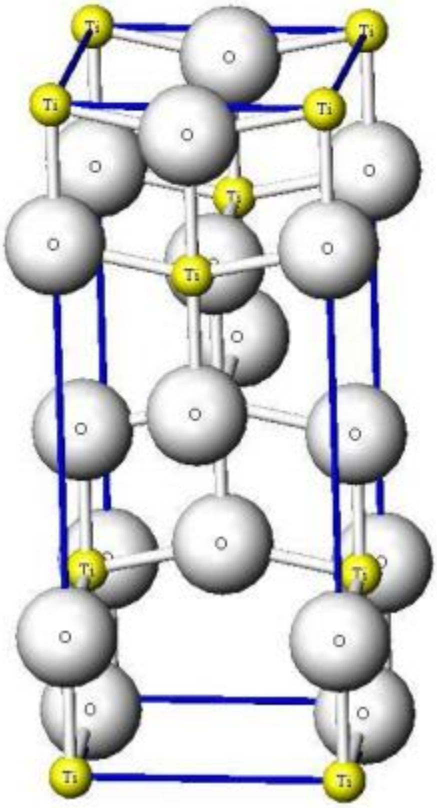

Figure 3 Conformation of crystalline TiO2 in the anatase form

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 photogenerated hole-electron couple that eventually results in the expulsion of oxygen atoms from the crystal.

By the formation of oxygen vacancies free electrons are made available resulting in n-doping of the material, whose electrical conductivity is increased. [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 State-of-the-Art Device

For the deposition of TiO2 solution, simply take the procedure for the construction of solar cells DSSC (Dye Sensitized Solar Cell) as a reference (described in the following – 2.4). The device structure is described in the following.[9]

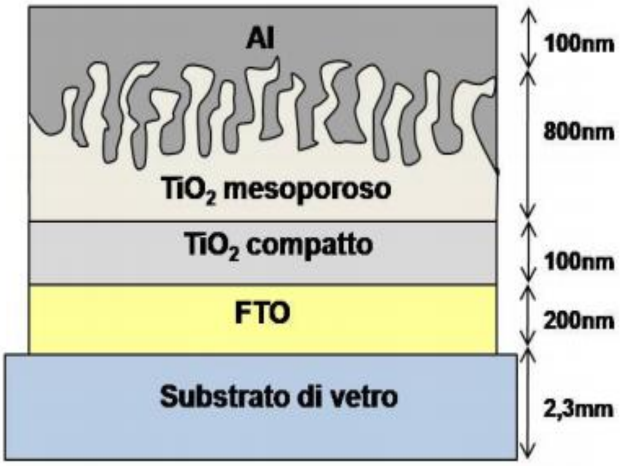

Figure 4 Structure of Vertical Devices based on TiO2[9]

The processes of deposition from titanium oxide solution need heat treatments at high temperatures (500C). This entails the replacement of commonly used indium tin oxide (ITO) transparent electrode with the less conductive, rougher FTO (Fluorine opded tin oxide), a similar with ITO, but capable of standing higher temperatures.

In solar cells, a monolayer of a dye material is adsorbed onto the TiO2 to act as a light antenna. To maximize the active surface, the TiO2 layer is mesoporous (hundreds of nm thick). When the antenna is photo excited, a hole/electron couple is created. On a very short time scale (sub-ps), electron transfer to TiO2 and hole transfer to a suitably selected hole transporting material (not shown in the picture) occurs due to favorable energy levels alignment. Then, photocurrent is read out of the cells as a consequence of photo generated hole and electrons collection respectively at aluminum and FTO side. Between the layer of mesoporous TiO2 and FTO, a compact layer of TiO2 is interposed to prevent unwanted recombination phenomena and to ensure selective collection of photo generated electrons at the FTO side. A surface treatment is applied to the mesoporous TiO2 layer before dye adsorption to passivate chemical defect and dangling bonds.

For what concerns the conductance change pixel, the light antenna and the holes transporter are not required, which leads to the structure tested in the previous thesis work by G.M. Salvi and sketched in fig. 5.

According to the work done by G.M. Salvi, the device demonstrated is quite good. Pixels are conductive, and the conductance has a significant improvement after UV light. What's more, the data shows the conductance change is stable in vacuum.

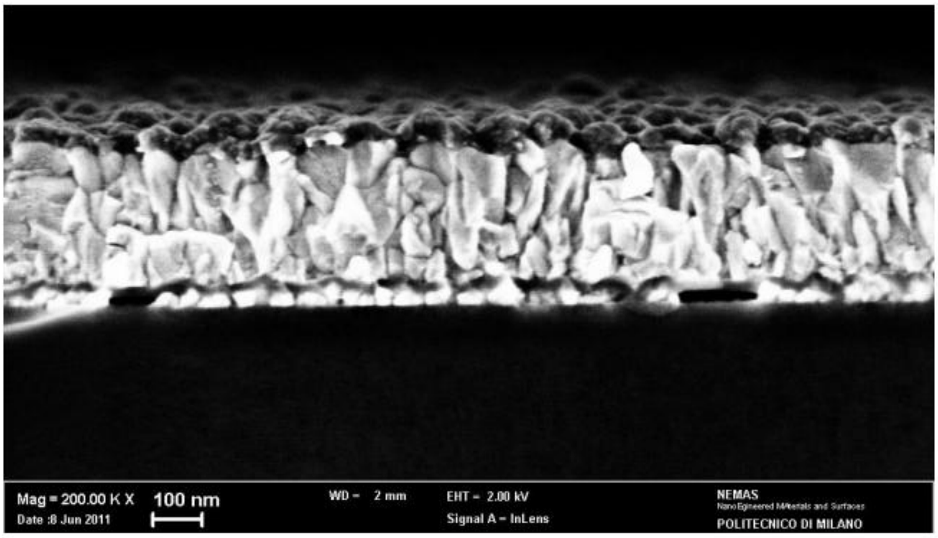

Figure 5. SEM image of a FTO layer (white) deposited on a glass base(dark, bottom). Above the FTO is deposited a thin film of TiO2 compact layer (upper dark layer). Note the considerable surface roughness of FTO.[5]

Moreover, since the working mechanism of the conductance change pixel is simpler compared to the case of solar cells, such a complicated structure for the TiO2 semiconductor layer, comprising a compact plus a mesoporous layer and undergoing surface passivation, could be not necessary and unfavorably for a wide application in industry.

2.3 Simplified device: introduction:

To explore possible improvements to the above mentioned device, we first tried to assess some key aspects of the device working mechanism..

1- **Is the mesoporous TiO2 layer really necessary?**

First of all, we aimed at understanding whether photo doping of the material was a bulk rather than a surface phenomenon. If it is a bulk phenomenon, then maybe a mesoporous layer with extended surface is not needed.

To answer this question we realized and characterized devices made of only a compact TiO2 active layer.

2- **Is the compact TiO2 layer really necessary?**

We explored the role of the compact TiO2 in addition to the mesoporous one, with the aim of checking if it was possible to get rid of it.

To answer this question we realized and characterized dev ices made of only mesoporous TiO2 active layer.

3- **Is the the TiCl4 surface passivation treatment really necessary?**

It increases the Complexity of fabrication and producer will prefer to skip this step.

To answer this question we compared the performance of devices with and without the surface treatment applied.

4- **Is the high processing temperature really necessary?**

In solar cells, TiO2 layers are annealed at very high temperature (500C) to i) evaporate residuals of organic precursors and ligands used for layer processing; ii) in the case of mesoporous layer , to promote the sintering of TiO2 nanoparticles (see experimental details in the following) for ensuring high conductivity and a well precise porosity of the material. In our application, specifications on material dark conductivity and porous morphology could be more relaxed than in the case of solar cells, thus enabling good results to be achieved with a low temperature processing.

Devices with different structure and processing condition are developed accordingly, a brief summary of the device we considered is listed as following:

Device	Structure	Cooking Temperature	TiCl4	Fact in consideration
0	Glass+FTO+Compact+Mesoporous+AL	500℃	YES	G.M. Salvi reference device
1	Glass+FTO+COMPACT+AL	500℃	/	Mesoporous absent
2	Glass+ITO+ Mesoporous+AL	500℃	NO	Compact+TiCl4 absent
3	Glass+ITO+ Mesoporous+AL	200℃	NO	Compact+TiCl4 absent Low Temprature
4	Glass+ITO+ Mesoporous+AL	200℃	YES	Compact absent LowTemperature
5	Glass+FTO+Compact+Mesoporous+AL	500℃	YES	Same device as reference
6	Glass+FTO+Compact+Mesoporous+AL	500℃	NO	TiCl4 absent
7	Glass+FTO +Mesoporous+AL	500℃	YES	Compact absent
8	Glass+FTO +Mesoporous+AL	500℃	NO	Compact +TiCl4 absent

Table 1 Device In consideration

During study, we fabricated device 1 to 8 when device 0 is the reference sample existed in literature only.

Device 1: Glass+FTO+COMPACT+AL

The mesoporous layer is removed, to check the importance of having extended interface to the photodoping effect.

Figure 6 Device1, without mesoporous layer

Device2/3/4: Glass+ITO+ Mesoporous+AL

Compact layer is removed. At the same time, devices are manufactured in different temperature: device2 is cooked at 500 degree while 3 and 4 are cooked at 200 degree.

It is expected to get information about the necessary of compact layer and influence of temperature.

Note the FTO layer is replaced by ITO, which has anyway very similar electrical behavior.

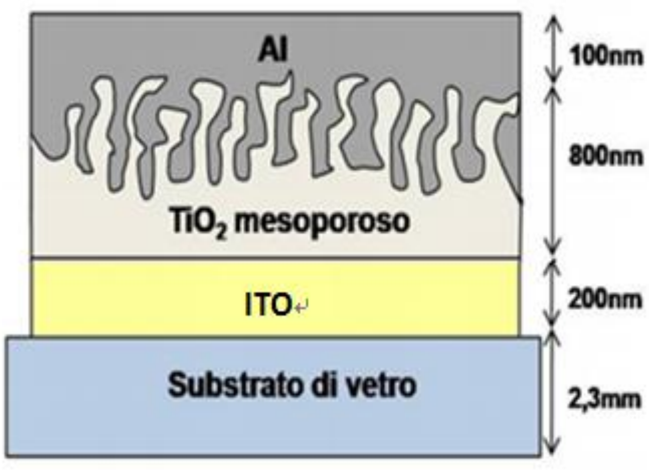

Figure 7 Device2/3/4 without compact layer

Device5/6: Glass+FTO+Compact+Mesoporous+AL

The structure of devices is same as the reference device.

Device 5 acts as real reference in our study, while device 6 missed the step of TiCl4 surface treatment.

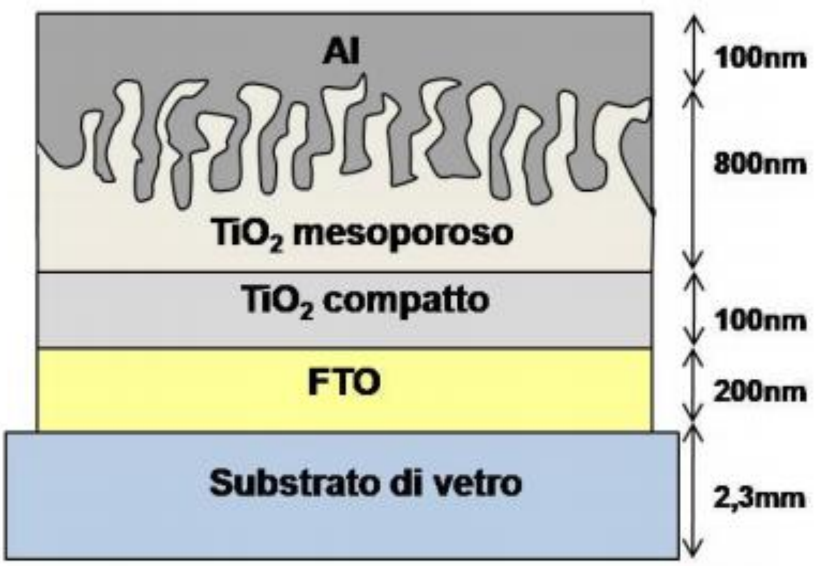

Figure 8 Device5/6 Complete devices

Device7/8: Glass+FTO+Mesoporous+AL

In compared with device 5/6, it provides information about the importance of compact layer.

Again, the device 7 completed the surface treatment process while device 8 skipped it.

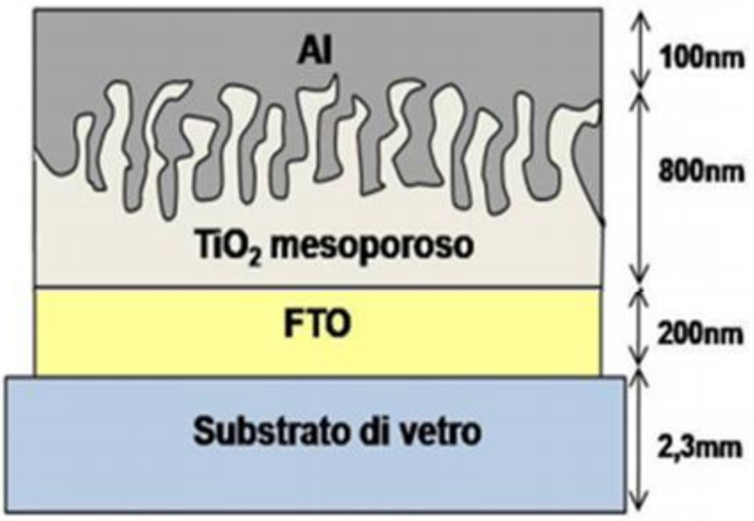

Figure 9 Device7/8 without compact layer

2.4 Device Preparation

The recipes for realization of each manufacturing step are listed in the following.

2.4.1 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). FTO/ ITO layer is used as a transparent electrode. Chemical Vapor Deposition introduces material in gaseous form and decomposed on the substrate surface later, which allows obtaining a solid deposit from a precursor molecular. So we can get a layer of FTO/ITO very durable and firmly anchored to the glass substrate.

Then FTO) /ITO coated glass substrates (15 Ω per sq Pilkington) were etched with zinc powder and HCl (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.

2.4.2 Compact TiO2 layer.

The substrates were then covered with a compact layer of TiO2 (~ 100 nm-thick).

Deposition of compact TiO2 was made by spray pyrolisis at 400 °C with oxygen as carrier gas, starting from a 1:10 by volume titanium diisopropoxide bis(acetylacetonate):ethanol solution.

The precursor of titanium oxide in contact with oxygen and at a temperature of 400 ° C is transformed into TiO2 and form a compact layer covering the slides. The samples are then left for a few minutes at this temperature and cooled very slowly, once they cool down to room temperature, stored in the glove box in a nitrogen atmosphere and waiting for the next step.

Device 2/3/4/7/8 they are device without compact layer and they will simply skip this procedure.

2.4.3 Mesoporous TiO2 layer.

A commercial Dyesol TiO2 paste (DSL 18NR-T), previously diluted in ethanol and ultrasonicated until complete mixing, was doctor bladed onto the compact TiO2 layer 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]

For device 1 which missed mesoporous layer will get rid of this step.

For low temperature devices: device 3 and device 4, the substrate will stay on 200 °C instead of 500°C.

2.4.4 Surface treatment with TiCl4.

After cooling, the substrates were soaked in TiCl4 solution (15 mM in water) and oven-baked 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.

For these without surface treatment: Device2, Device 3, Device 6 and Device 8 will skip this procedure.

The image taken by SEM shown in Figure 10 is possible to observe the structure of the cutting device with TiO2 on mesoporous TiO2 compact and FTO.

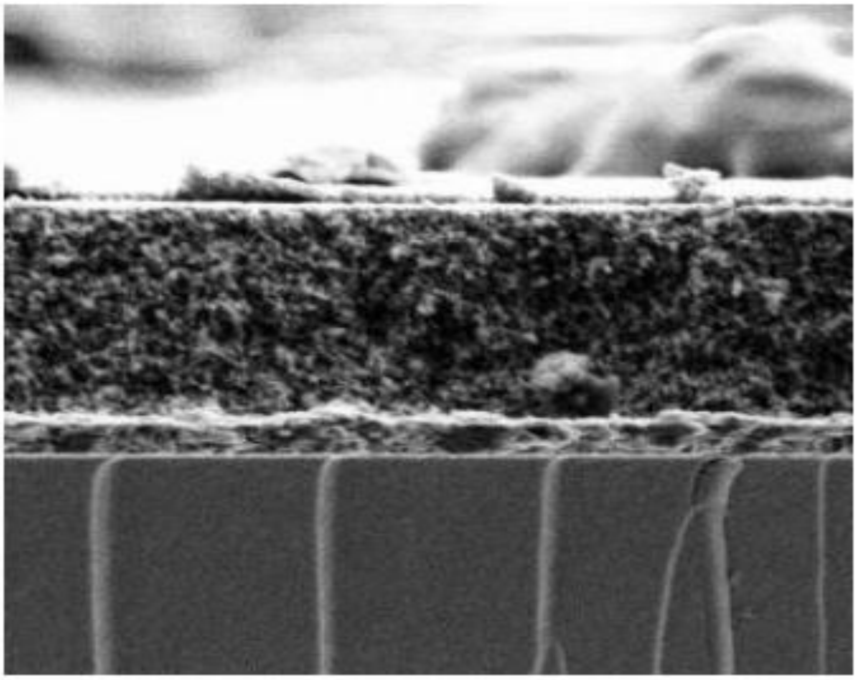

Figure 10. SEM image of a device with mesoporous TiO2. Starting from the bottom is known as glass, FTO, the layer of TiO2 compact and subsequently the very thick layer of mesoporous TiO2.

2.4.5 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.

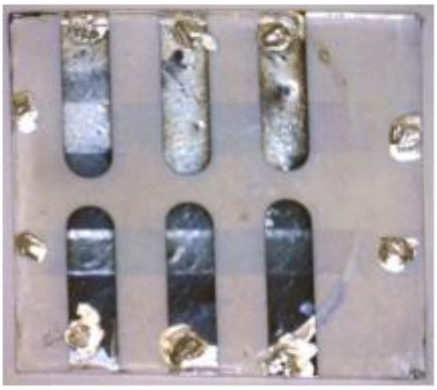

Figure 11, Prepared Device with Al on top

2.4.6 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, 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.

3. Experimental Results

3.1 Basic Steps Introduction:

Treatment	**Atmosphere**	**Factor of variation of the average current**
UV Light **Led 370nm UV,10s,84uW**	Vacuum	1000
	Air	<2
Temperature treatment **1 hour, 80 Degree**	Glove box	1/10
	Air	1/1000

Table 2 devices conductivity analyzed following characterizations carried out in different atmosphere

Thanks to the work of G.M. Salvi, we can see vacuum is the best working environment during UV exposure and air during the heat treatment for recovery.

After device preparation:

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

   As a result of the heat treatment, passivation of oxygen vacancies is expected.

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

   Obviously, in vacuum It is considerably less probabily that oxygen atoms expelled by absorption of a photon are replaced by other atoms present in the measurement environment. The vacuum chamber in CNST electronic lab provides a low pressure environment under 10E-5 ρgh with a pump working at 1500HZ.

3. Measure the device in dark

   To check the connections and the original conductance, it is necessary to measure the device in dark. The result would be important reference of the change of conductance after UV light.

4. Apply a short UV light, 2s for instance

   During our study, we use the lamp which provides 365nm UV light, correspond to 3.4eV, a little bit higher than the energy gap(3.2Ev) of the material. To avoid the power of UV light damage the device, it is better to apply the light gradually until it reaches saturation. 2 second per time for instance. Measure it immediately.

5. Apply a longer uv light, detect V-I curve.(may several time)

6. . Leave in vacuum for at least one day. Measure again.

   Devices will be left in vacuum and dark situation for a period to check the stability. The conductivity of device is changing with time.

Optional:

7. Apply UV light again, measure

In case of necessary, we can repeat the measuring process to same device.

8. Detect after days as well or after air exposure.

3.2 Test Runs Based on Different Factors

To explore the possibility of simplification, we make devices in various situation and run several measuring based on 4 considerations.

A. If it is possible to make device without Mesoporous layer
B. if it is possible to make device without TiCl4 surface treatment
C. If it is possible to make device without compact layer
D. Is it possible to achieve satisfactory device behavior by low temperature (200C) processing?

The specific result is demonstrated as following:

3.2.1 TiO2 Mesoporous Layer

Device information:

1	Glass+FTO+COMPACT+AL	500	/	Mesoporous Absent

Measuring condition: Vacuum, Dark

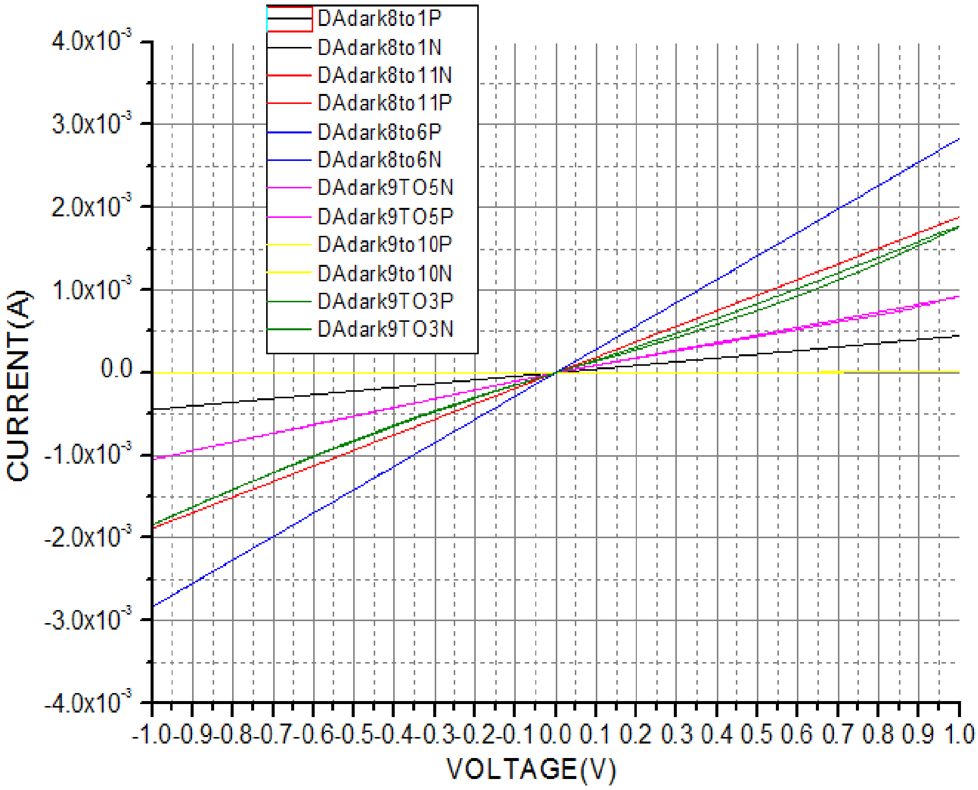

Figure 12. I-V Curve OF Device 1 measured in dark

As we can see from the plot, the 6 channels of the device in dark condition is not uniform. But the current is in the range of 10 to -3 order.

Then we apply UV light to the device gradually, and leave device in dark and vacuum for a period. Unfortunately, we did not see any change during the whole measuring process.

For a specific pixel 8to6, the V-I curve is plotted as flowing:

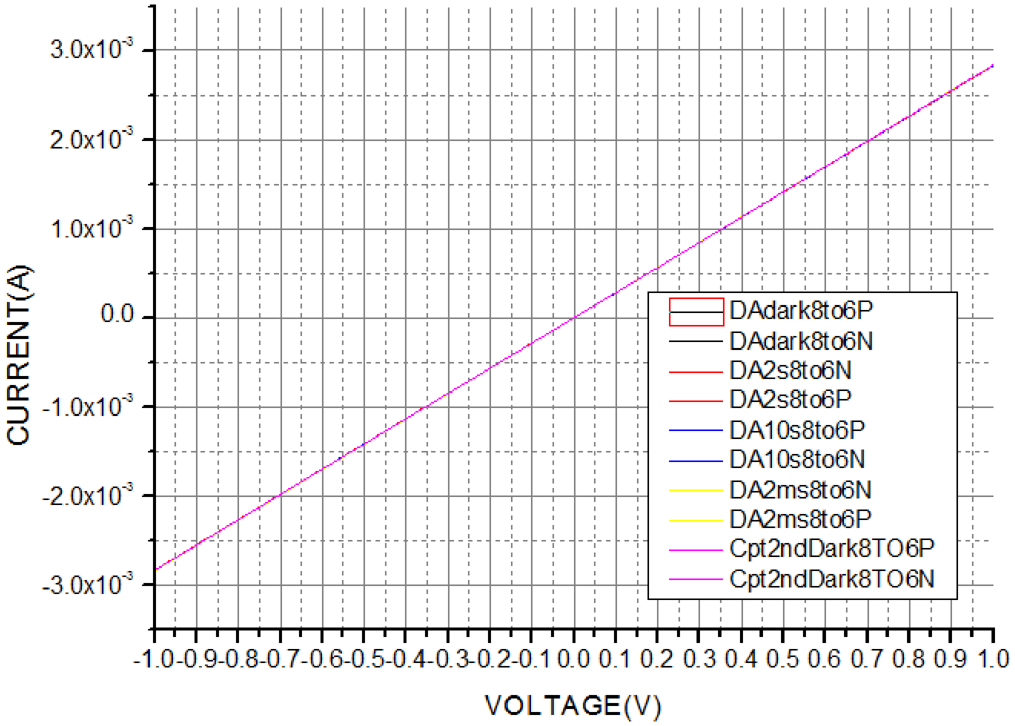

Figure 13 I-V Curve OF Device 1,pixel 8-6, measured in dark, after 2 seconds UV exposure,10s exposure,2 minutes exposure, and 2nd measuring in dark.

Comment:

As we can see, the device does not work in this case, which means the mesoporous layer is compulsory for the device.

Higher conductivity conductivity compared to reference device can be attributed to fabrication process of compact TiO2 by spray pyrolisis which, by the literature, is known for leading to highly defective films with already high n-doping level (high number of native oxygen vacancies). At the same time, no change at all in conductance after UV light exposure suggests extended surface, i.e. a mesoporous layer, is required for sizable photodoping effect to be measured.

3.2.2 TiCl 4 Surface Treatment

3.2.2.1 Device with TiCl4 Surface Treatment

Device information:

5	Glass+FTO+Compact+Mesoporous+AL	500℃	YES	Reference Device

Measuring condition: Vacuum, Dark

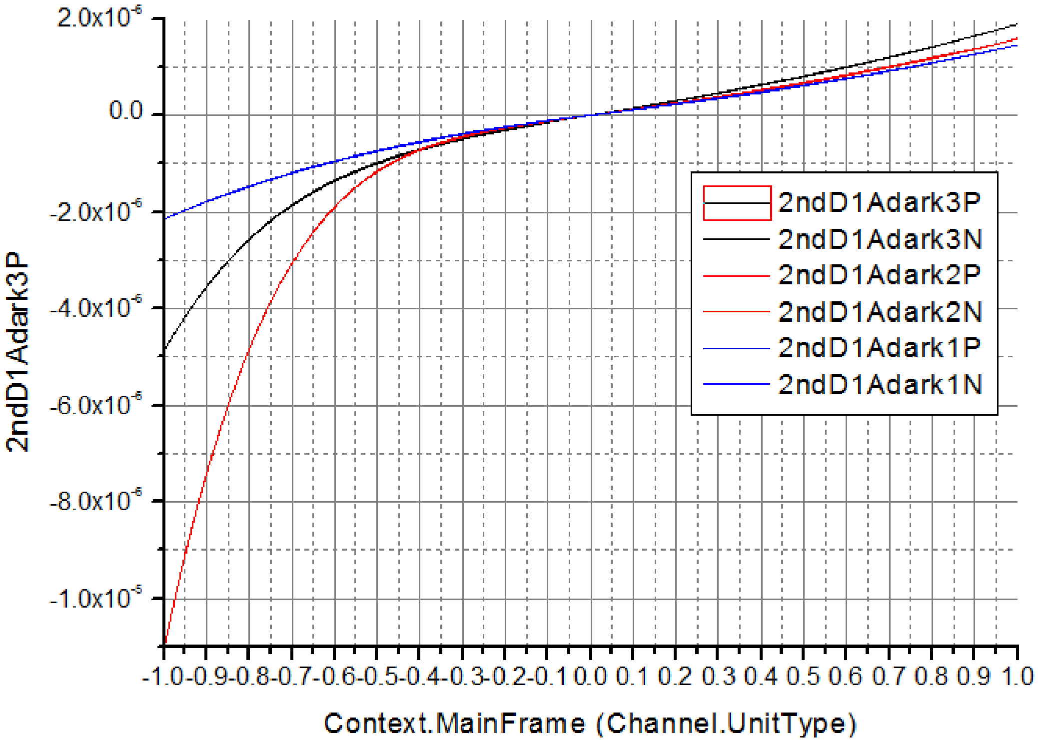

Figure 14 I-V Curve OF Device 5 measured in dark

Measuring condition: Vacuum, 6s UV light

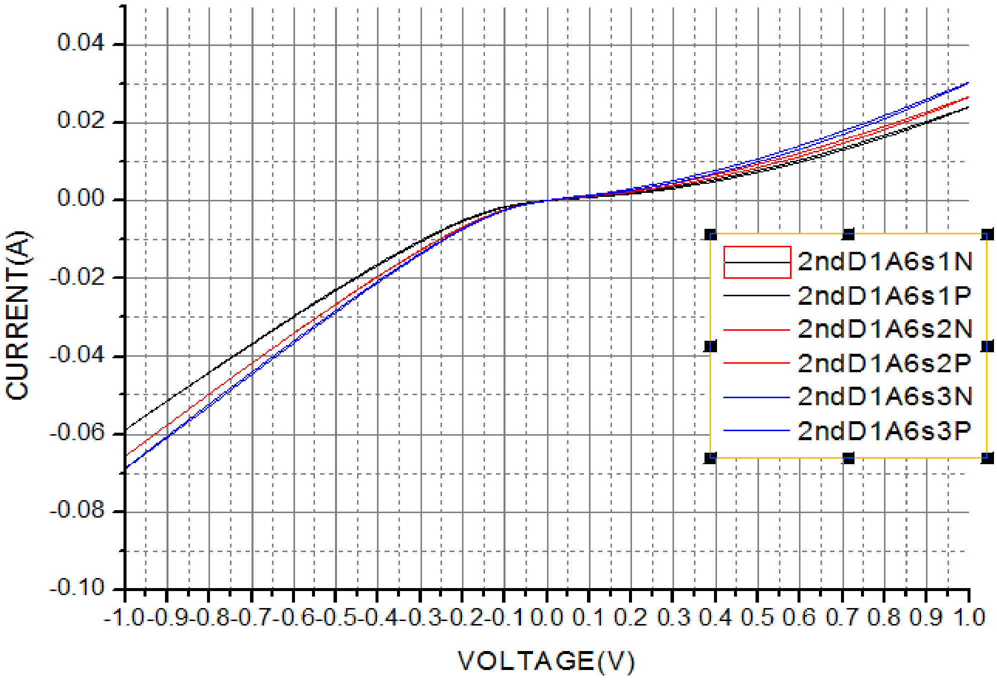

Figure 15 I-V Curve OF Device 5 measured after 6 seconds UV exposure

Measuring condition: Vacuum, 30 hour after 6s UV light.

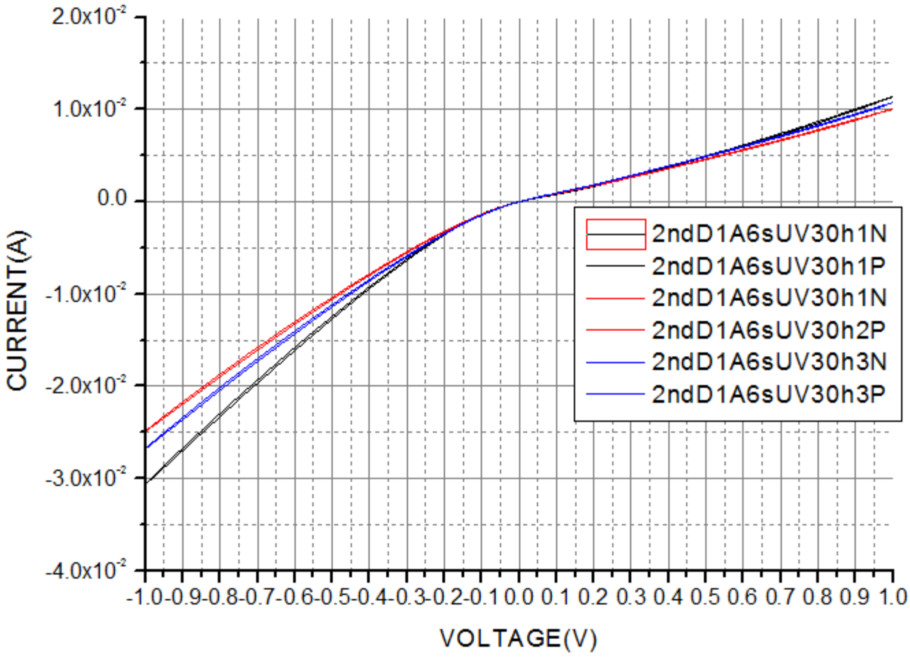

Figure 16, I-V Curve OF Device 5 measured 30 hours after 6 seconds UV exposure

As we can see from the figures:

1. The conductivity is increased from 10E-6 TO 10E-2 after 6 second UV light.
2. The conductivity decreased after 30 hours, but still in the same order. Hence we can say it is almost stable in dark and vacuum environment.

   Comment: the results proposed by G.M. Salvi have been reproduced.

3.2.2.2 Device without TiCl4 surface treatment

Device information:

6	Glass+FTO+Compact+Mesoporous+AL	500℃	NO	TiCl4 absent

Measuring condition: Vacuum, Dark:

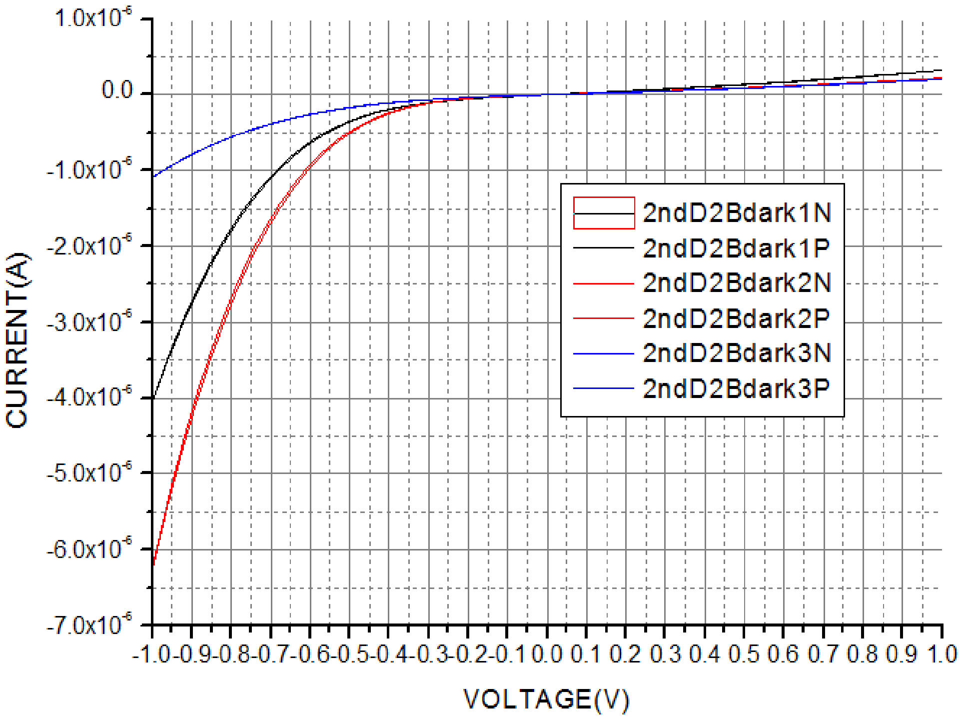

Figure 17, I-V Curve OF Device 6 measured in dark

Measuring condition: Vacuum, 5s UV light:

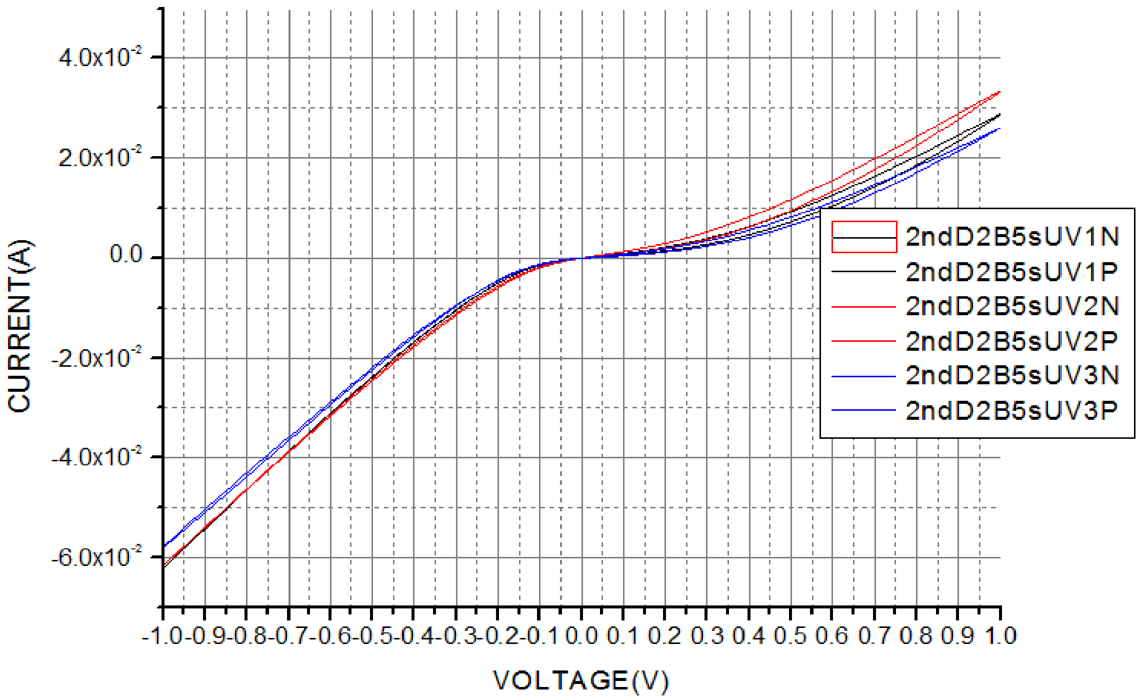

Figure 18 I-V Curve OF Device 6 measured after 5 seconds UV exposure

Measuring condition: Vacuum, 42 hours stay in vacuum and dark after 5s UV light:

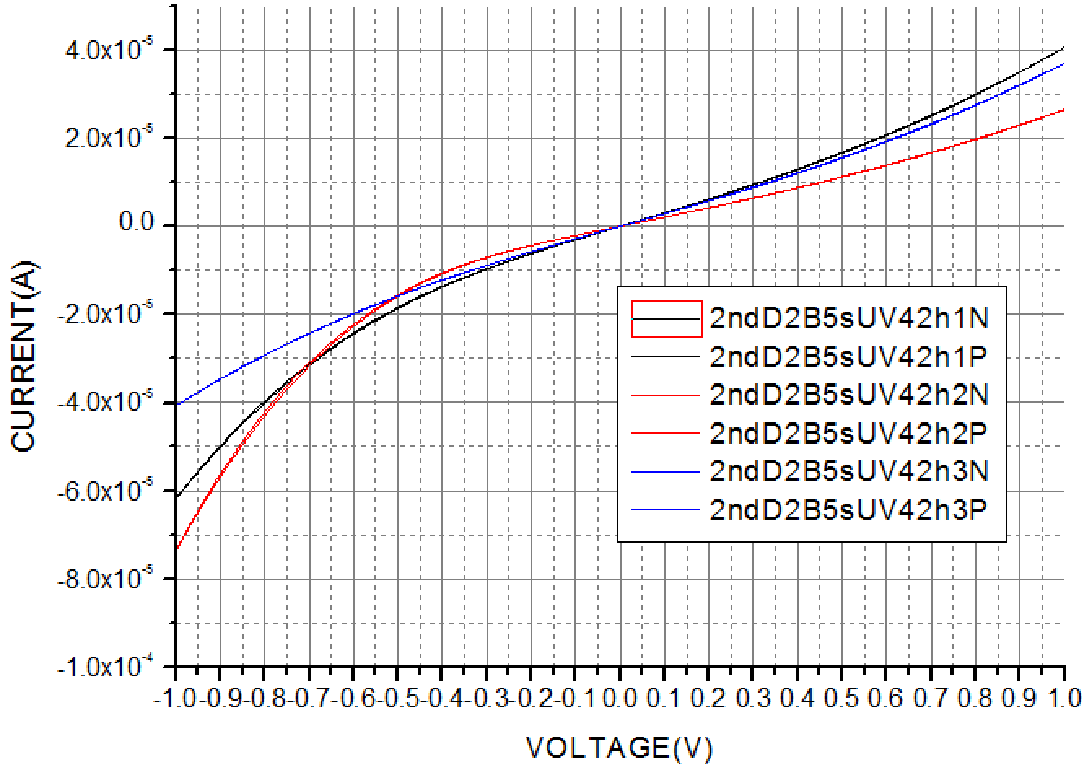

Figure 19 I-V Curve OF Device 6 measured 42 hours after 6 seconds UV exposure

1. The conductivity is increased from 10E-6 TO 10E-2 again after 5 second UV light. More or less similar to reference device.

2. The conductivity decreased a lot after hours. In the case of 42 hours, the maximum value decreases from 10E-2 to 10E-5 compared with the data measured after UV exposure.

3. It is predictable that the conductivity will continue decrease if we leave the device in dark and vacuum environment. Hence, the device shows a reversible change in conductivity.

Comment:

A possible explanation is TiCl4 have an effect on the stability and reversibility of the device, which need more investigation to support.

3.2.3. TiO2 Compact Layer

3.2.3.1 Device without Compact A

Device information:

7	Glass+FTO +Mesoporous+AL	500℃	YES	Compact

Device in reference:

5	Glass+FTO+Compact+Mesoporous+AL	500℃	YES	Classic device

Measuring condition: Vacuum, Dark

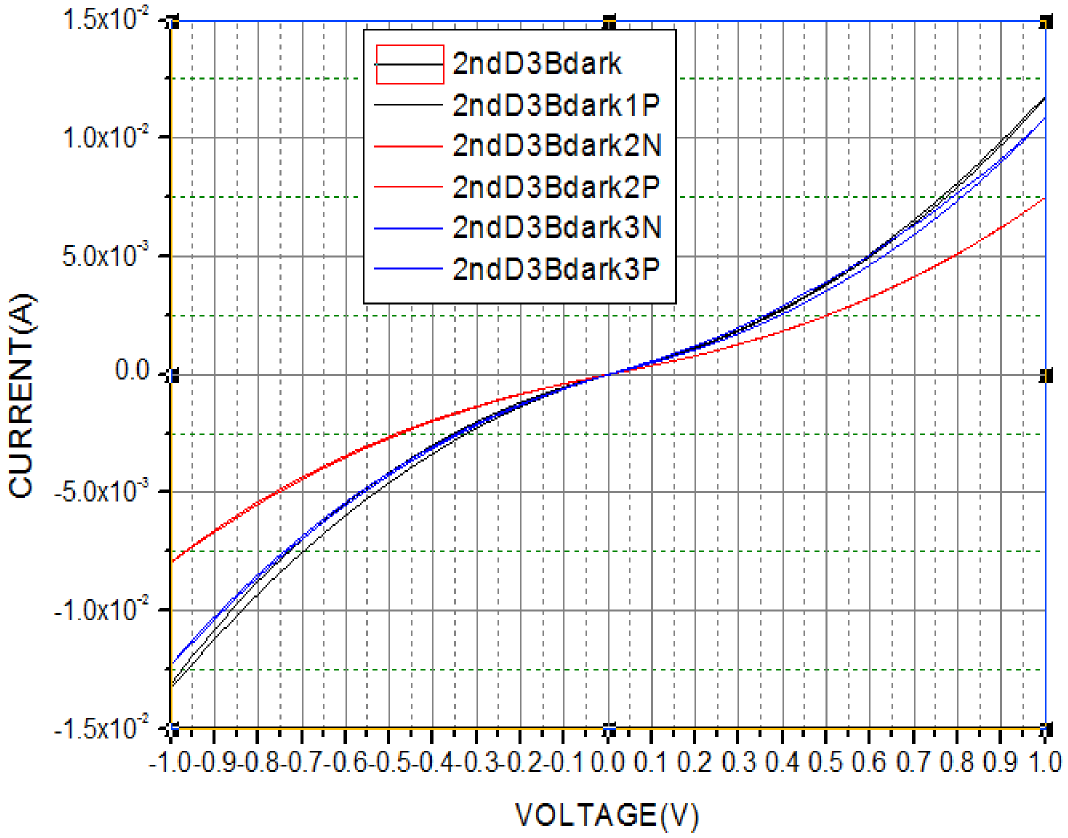

Figure 20, I-V Curve OF Device 7 measured in dark

Measuring condition: Vacuum, 8s UV light

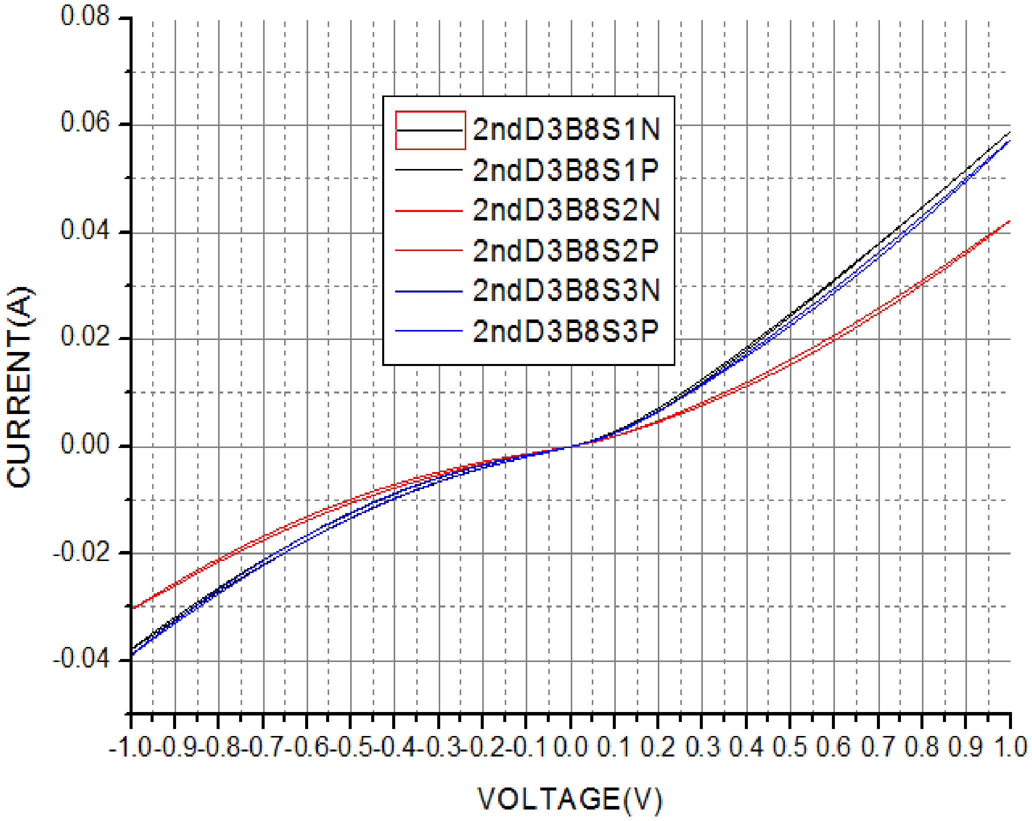

Figure 21. I-V Curve OF Device 7 measured after 8 seconds UV exposure

Measuring condition: Vacuum, 28 hours in dark and vacuum after 8s UV light

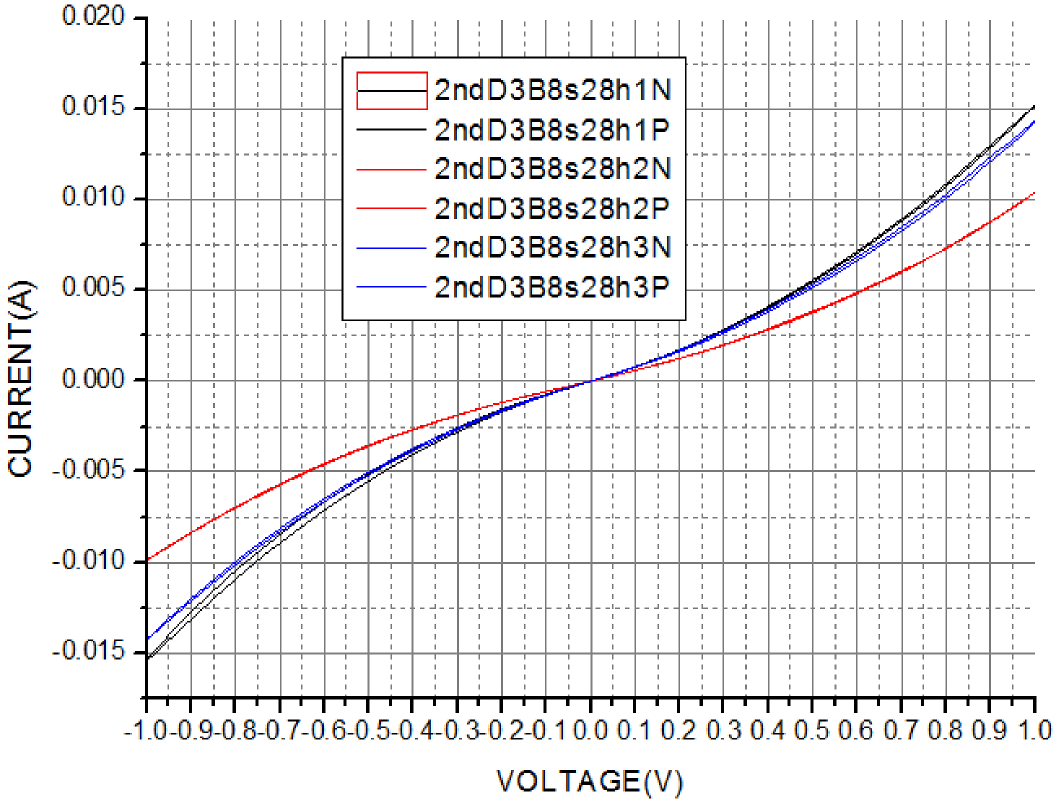

Figure 22, I-V Curve OF Device 7 measured 28 hours after 8 seconds UV exposure

We obtain:

1. A noticeable point of this device is that: the original conductivity of pixels is quite high compared with other devices we have seen before. Around 10E-2 (A/V) in dark situation. Instead of 10E-6 (A/V) in the case of device 5.
2. After UV exposure, the conductivity is increased but not significant.
3. It is difficult to tell if the device is stable or not as the improvement was few.

Comments:

A possible explanation is that the missing of compact layer may contribute to the short circuit of device.

The total conductivity between 2 layers of the device may consist of 2 parts: a G_P due to photo doping and a fixed G_O. When the conductivity of other components is high, the total conductivity is dominated by G_O and we cannot observe the significant change due to UV light.

3.2.3.2 Device without Compact Layer B1

Device information:

8	Glass+FTO +Mesoporous+AL	500℃	NO	Compact +TiCl4 absent

Device in reference:

6	Glass+FTO+Compact+Mesoporous+AL	500℃	NO	TiCl4 absent

Measuring condition: Vacuum, dark

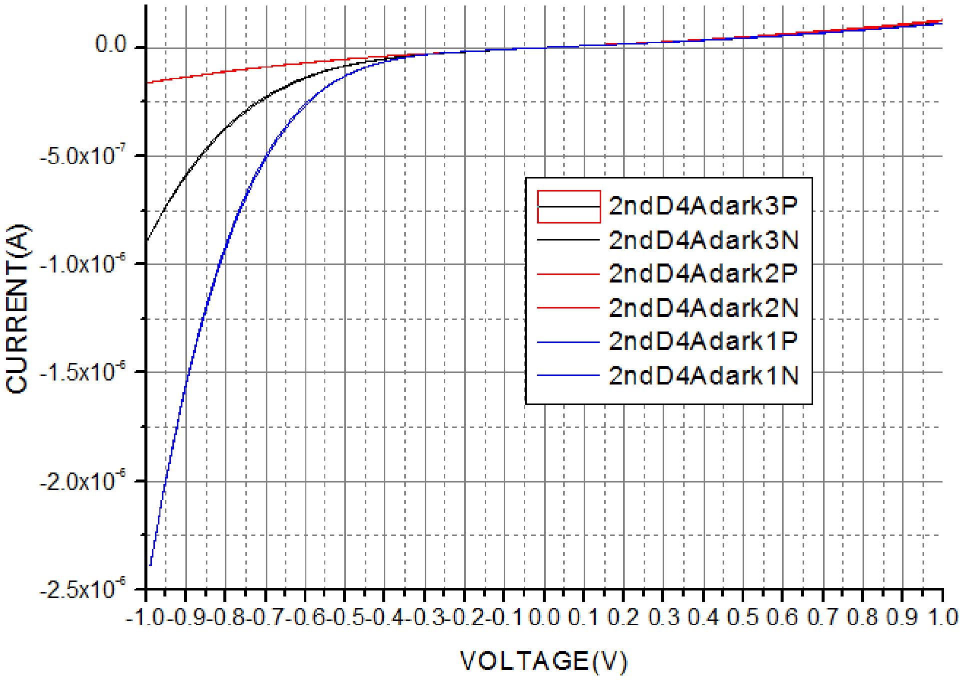

Figure 22 I-V Curve Of Device 8 measured in dark

An overview of the 2^{nd} pixel in different case:

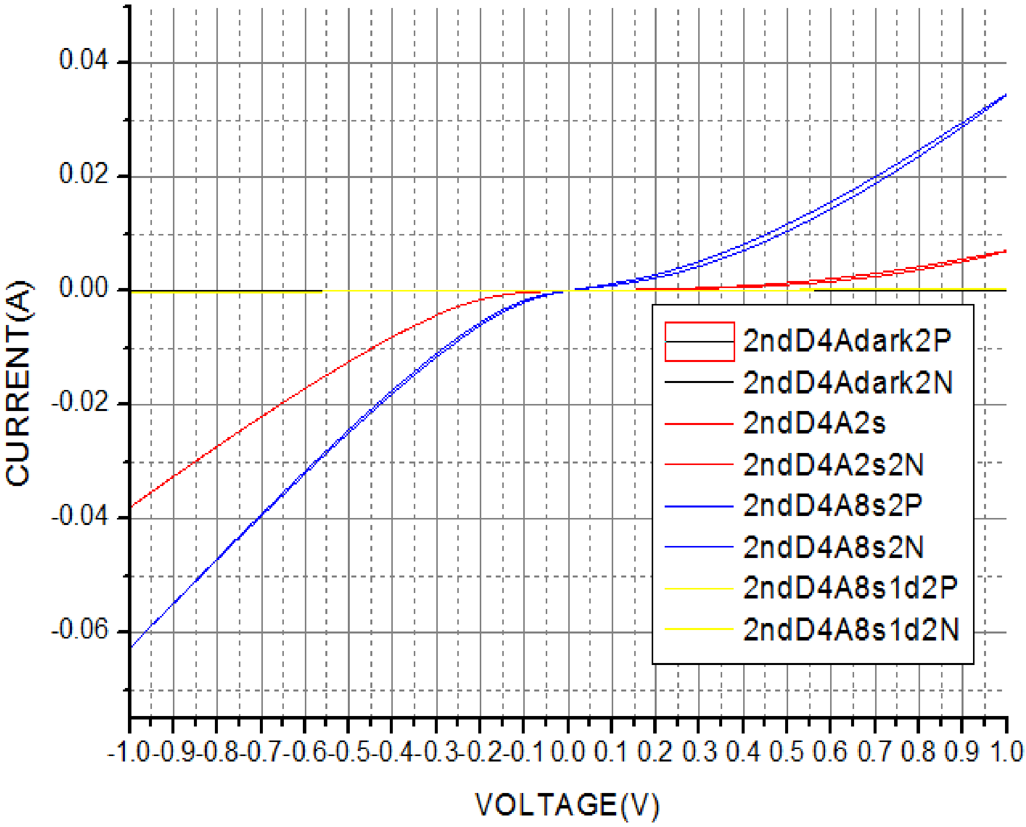

Figure 234. I-V Curve Of Device 8_1,2^{nd} pixel, measured in dark, after 2 seconds,8 seconds,1 day after 8seconds UV exposure.

3.2.3.3 Device without Compact Layer B2

Device information:

8	Glass+FTO +Mesoporous+AL	500℃	NO	Compact +TiCl4 absent

Device in reference:

6	Glass+FTO+Compact+Mesoporous+AL	500℃	NO	TiCl4 absent

Measuring condition: Vacuum, dark

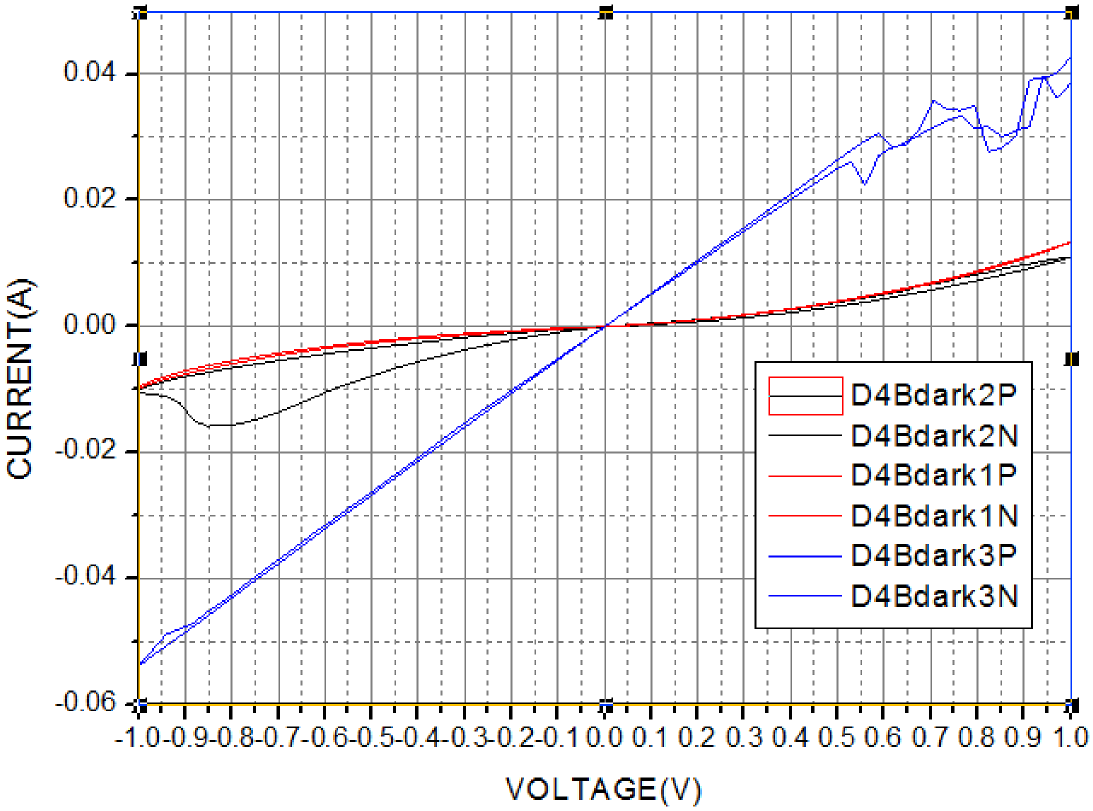

Figure 25. I-V Curve OF Device 8_2, measured in dark

An overview of the 1st pixel in different case:

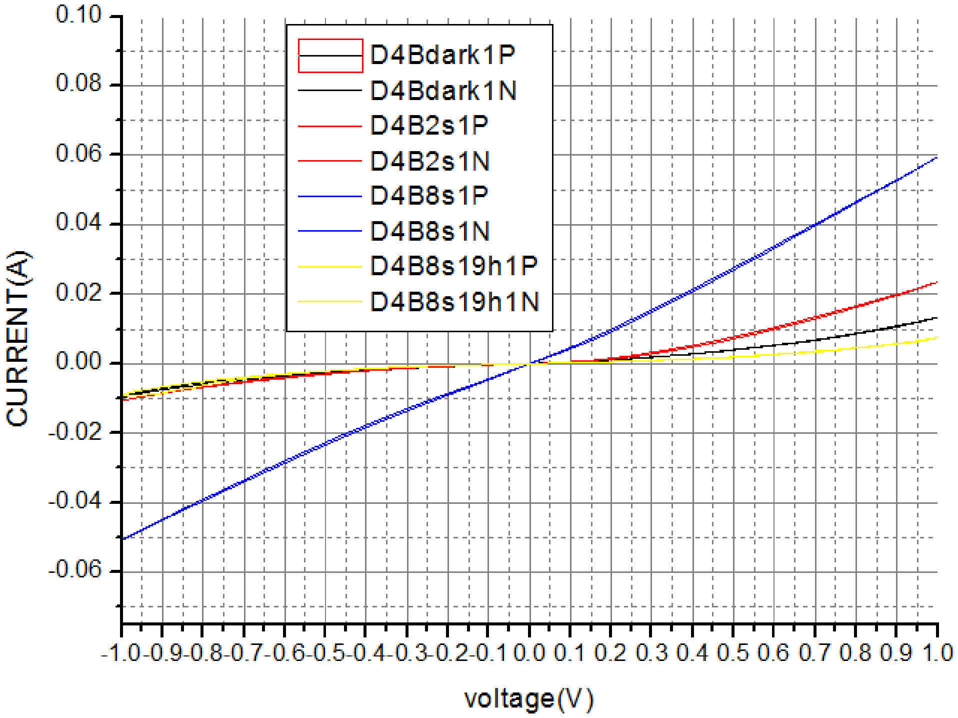

Figure 24 I-V Curve OF Device 8_2,1st pixel, measured in dark, after 2 seconds, 8 seconds,19 hours after 8seconds UV exposure

It is interesting to see 2 identical device behaviors different in same experiment environment.

1. Two devices in have exactly same physical structure and was fabricated at same time and environment. Device in 3.2.3.2 is starting from 10E-6 which is similar to the value of classic device, while the other one is around 10E-2, more or less same to the device in 3.2.3.1(Device 7).

2. The device is not stable. The conductivity is decreasing with time.

Comments:

A possible explanation is that the missing of compact layer may contribute to the short circuit of device in a certain extent but not definitely.

Again, the device is not stable and shows a reversible change in conductivity.

3.2.4 Temperature Treatment

3.2.4.1 High Temperature: D2

Device information:

2	Glass+ITO+ Mesoporous+AL	500℃	NO	Compact+TiCl4 absent

Measuring condition: Vacuum, dark

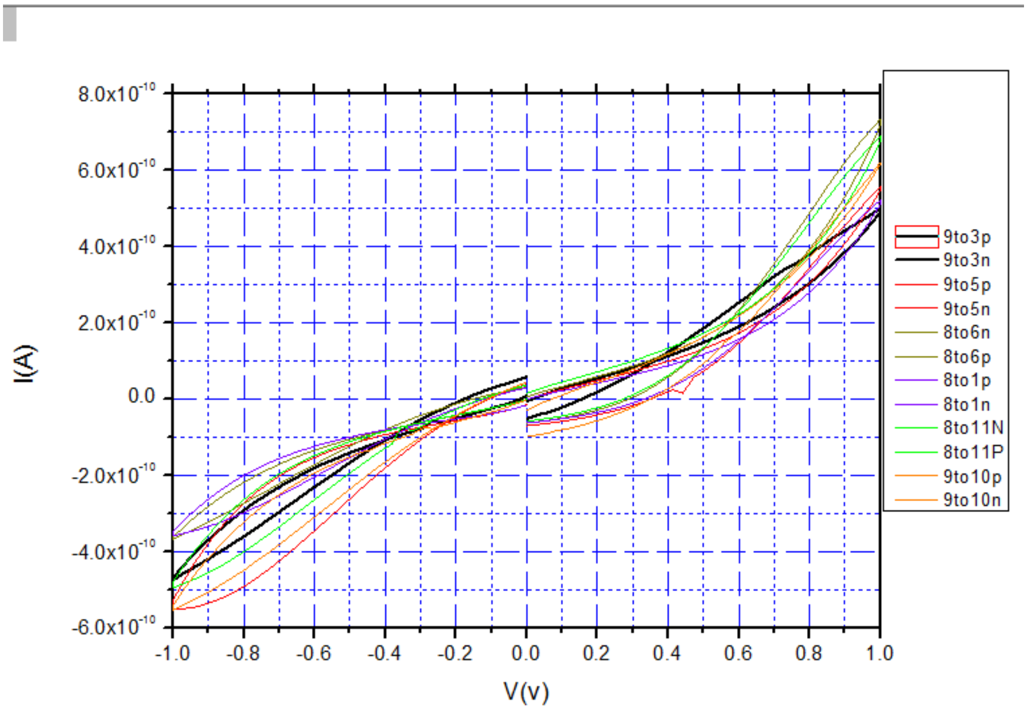

Figure 25 I-V Curve OF Device 2, measured in dark

Measuring condition: In vacuum, after 8s UV light

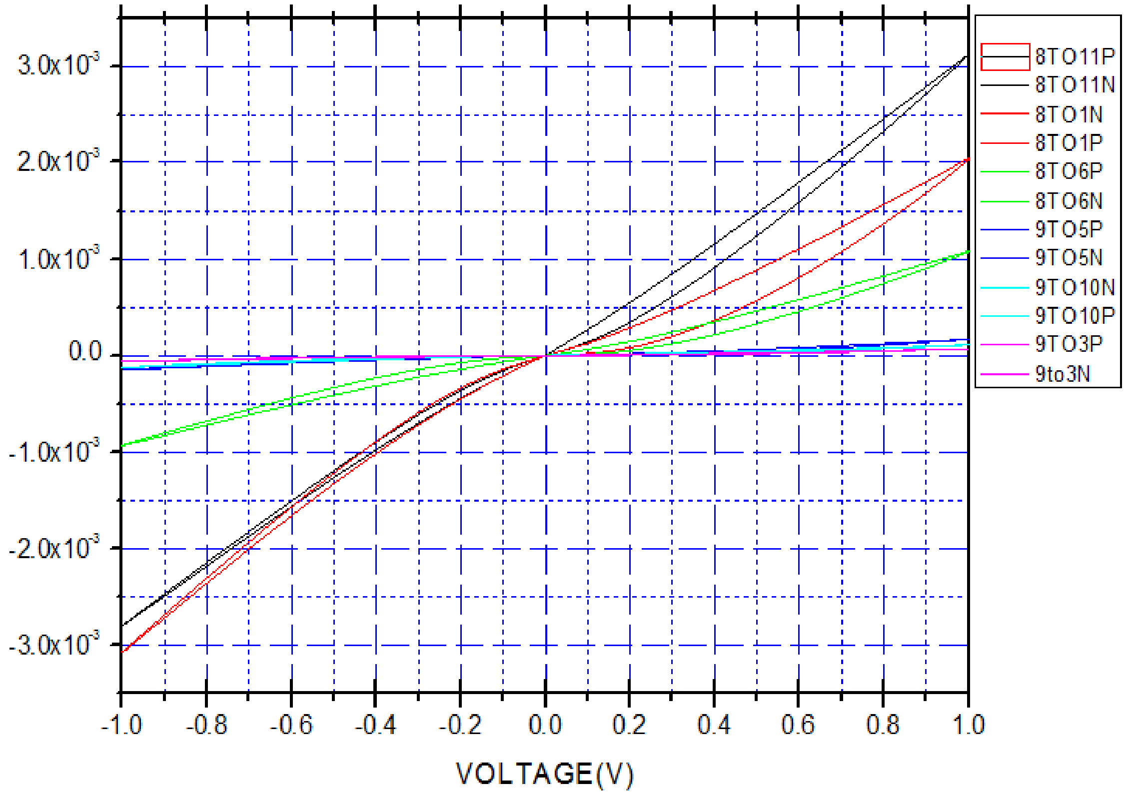

Figure 28. I-V Curve OF Device 2, measured after 8seconds UV exposure

Measuring condition: Pixel 8-11 Overview

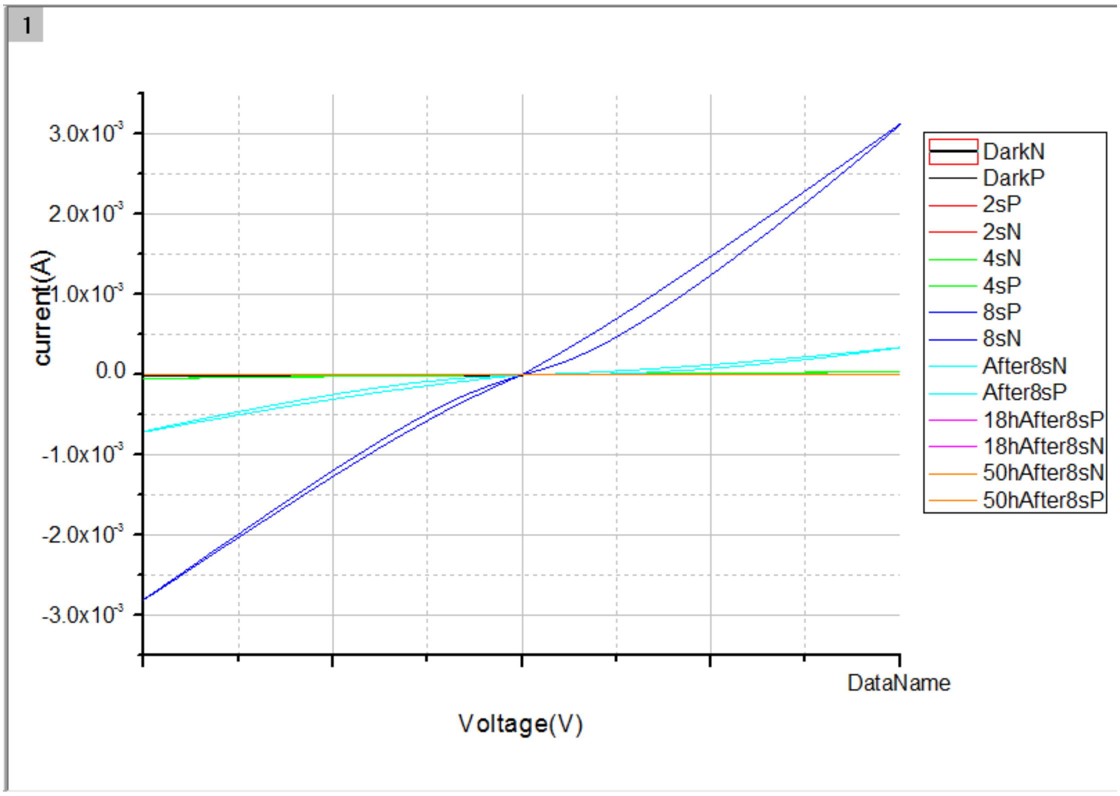

Figure 29 I-V Curve OF Device 2, average pixel 8-11, measured in dark, after 2seconds,4 seconds, 8 seconds UV Exposure, minutes, 18hours,50 hours after 8 seconds UV exposure.

Measuring condition: Pixel 8-11 Stability check

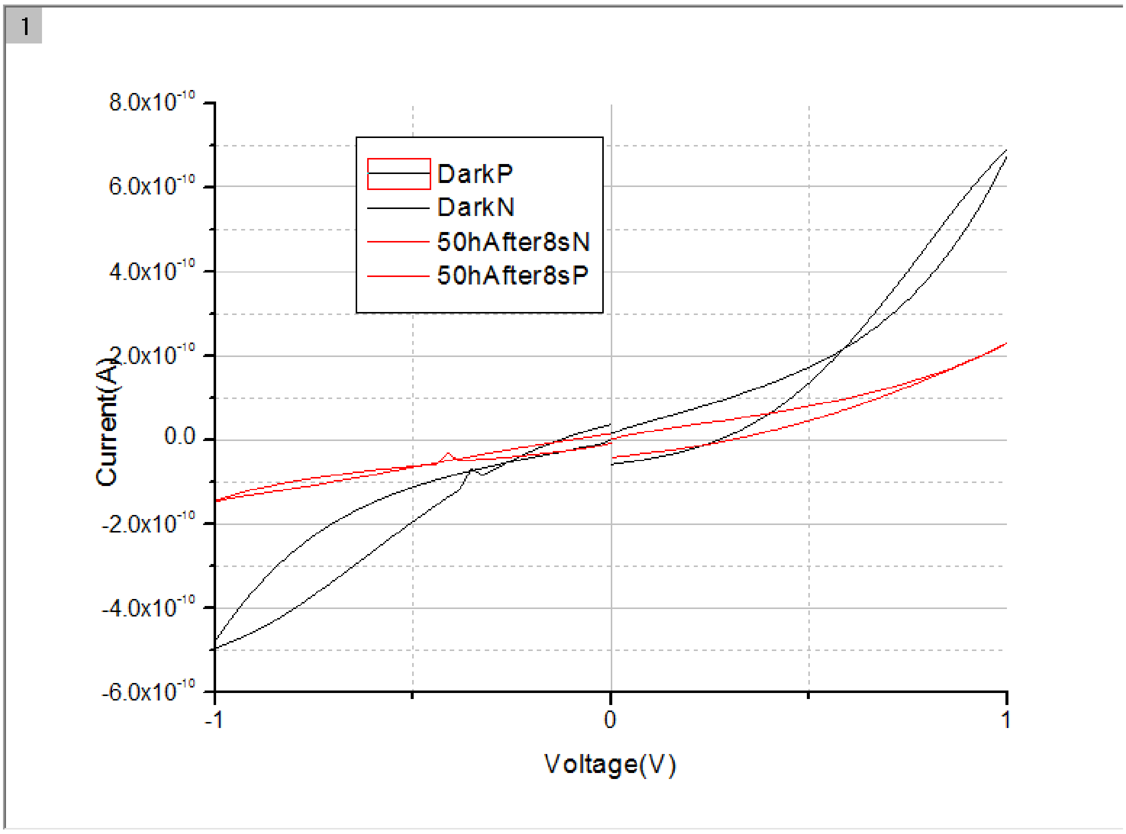

Figure 30. I-V Curve OF Device 2, average pixel 8-11, measured in dark and 50 hours after 8 seconds UV exposure.

1. After 8s UV, the current do not increased any more compared to 4S. Hence It is supposed to have been saturated.

2. The conductivity is starting from 10E-10 to10E-3 after 8s UV light

3. It is obvious that the device is not stable; actually, the conductivity is changing spontaneously. During measuring, we can see the maximum channel is depending on time: Always the first pixel measured have the maximum conductivity.

Comments:

The final conductivity is even lower than in original dark situation after 50 hours. This is possible due to the environment during first measurement is not dry or vacuum enough. , The device is not stable and shows a reversible change in conductivity.

3.2.4.2 Low temperature device A

Device information:

3	Glass+ITO+ Mesoporous+AL	200℃	NO	Compact+TiCl4 absent Low Temprature

Measuring condition: Vacuum, dark

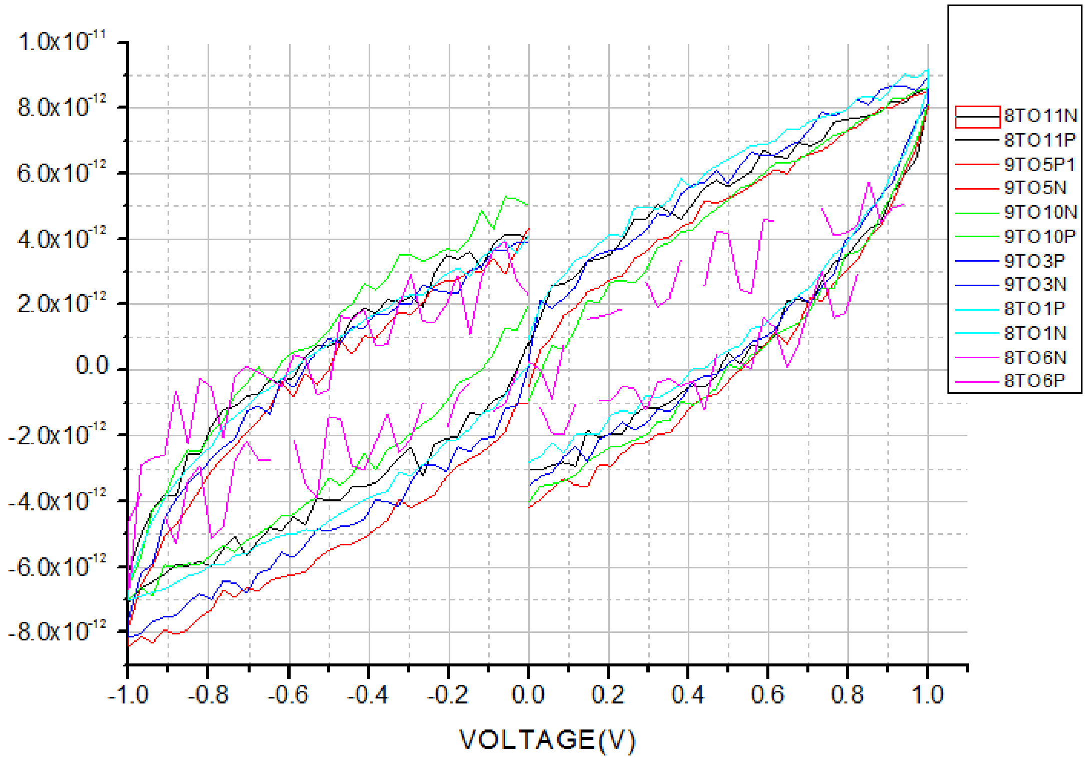

Figure 31. I-V Curve OF Device 3, measured in dark

Measuring condition: Vacuum, after 8seconds UV light

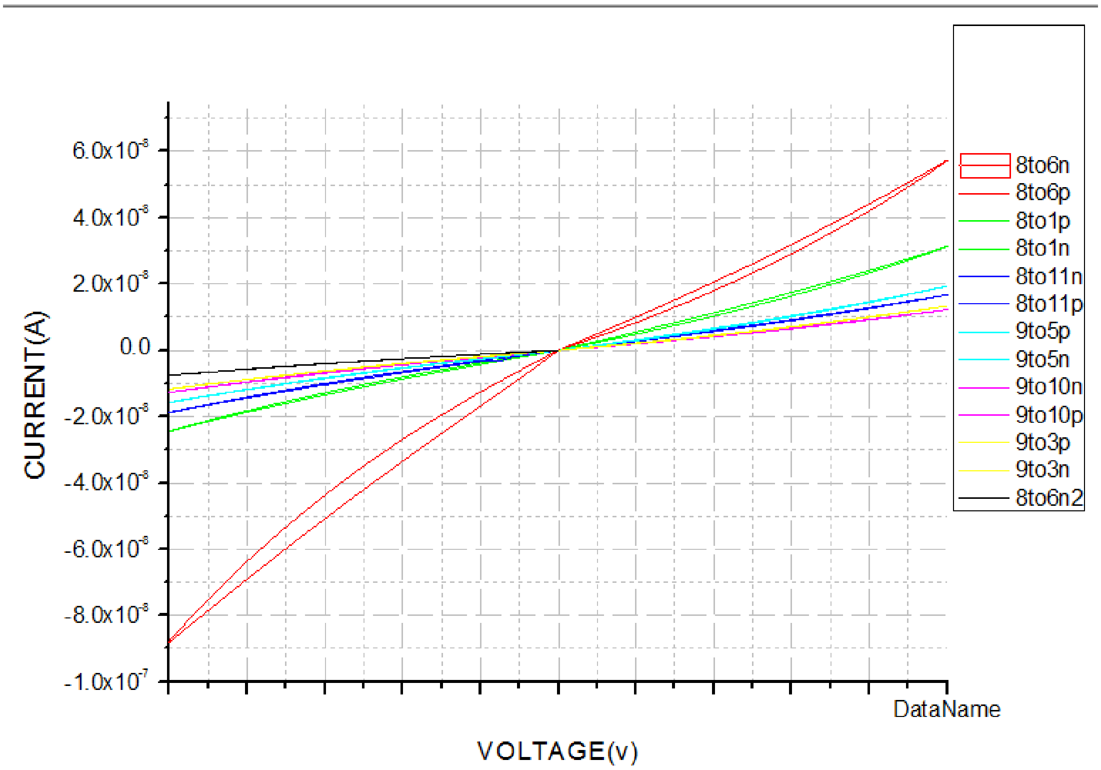

Figure 32. I-V Curve OF Device 3, measured after 8 seconds UV exposure

Measuring condition: pixel 9-5 overview

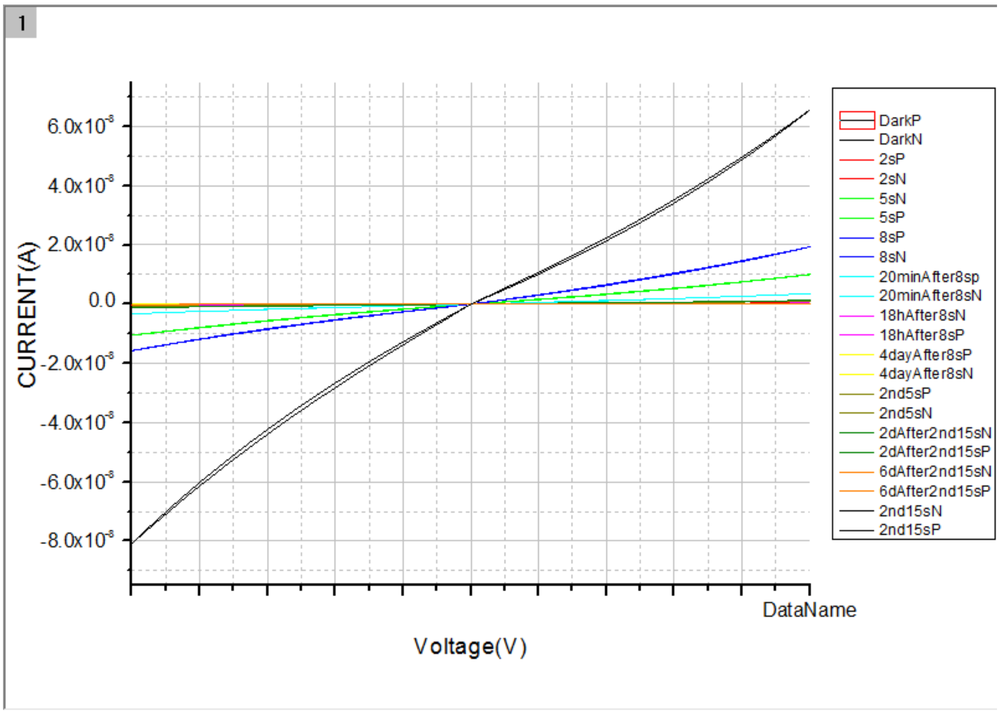

Figure 26. I-V Curve OF Device 3, average pixel 9-5, measured in dark, after 2seconds, 5 seconds, 8 seconds UV Exposure; 20minutes, 18hours,4 days after 8 seconds UV exposure; Second UV Exposure with 5 seconds,15 seconds; and 2 days,6days after second UV exposure.

Measuring condition: stability check of pixel 9-5

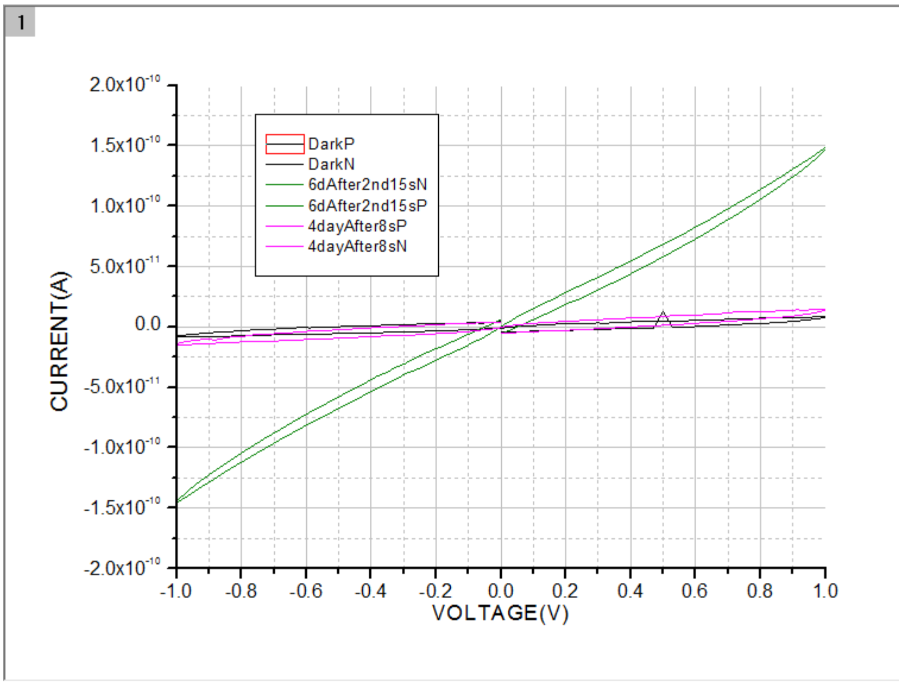

Figure 34. I-V Curve OF Device 3, average pixel 9-5, measured in dark; 4 days after 8 seconds UV exposure; 6days after second UV exposure.

Measuring condition: reversibility check of pixel 9-5

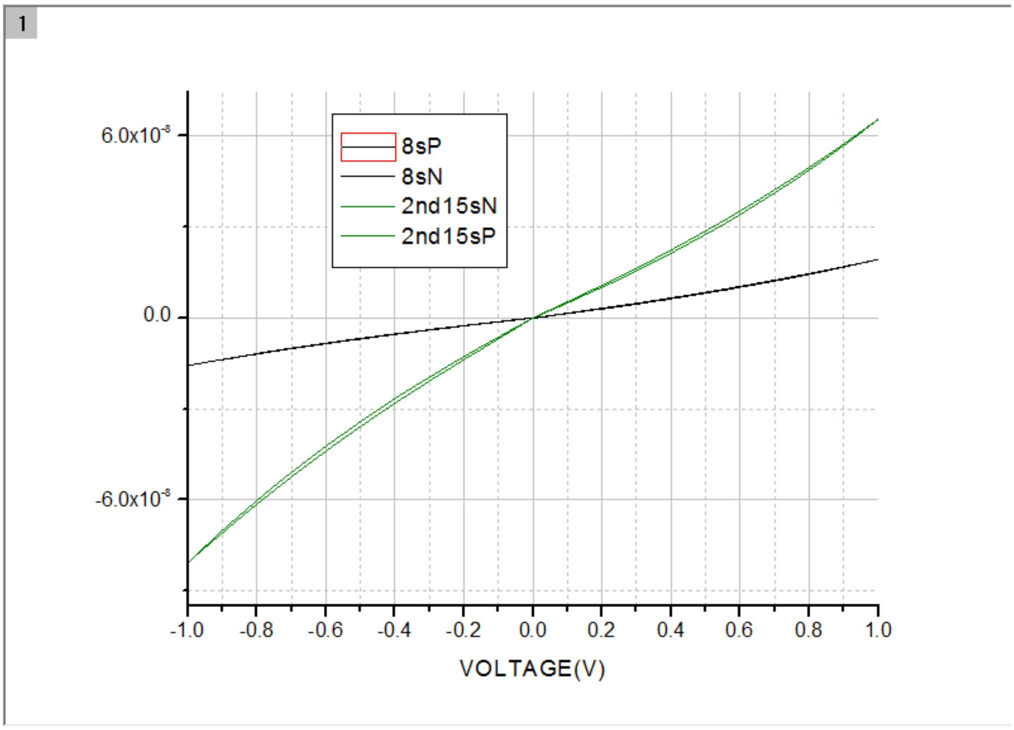

Figure 35. I-V Curve OF Device 3, average pixel 9-5, measured after 8 seconds UV Exposure; and Second UV Exposure with 15 seconds.

1. The conductivity is starting from 10E-12 to10E-8 after 8s UV light, which is lower than in high temperature case.

2. It is obvious that the device is not stable. After 4 days in dark and vacuum, the conductivity reduced until the same order of starting value.

3. Pixel 9-5 is the average one in this device. According to its performance, the device may be reversible. The second 15second UV light is applied after the device exposure 10 seconds UV and stay in Vacuum for 4 days. But It do have some difference. After 6 days, the value stay around 10E-10 (A/V), which are still 2 orders higher than starting value 10E-12(A/V).

Comments:

It indicated that: devices treated in high temperature tend to be higher conductive.

Devices are not stable without TiCl4 surface treatment and show a reversible change in conductivity.

3.2.4.3 Low temperature device B

Device information:

4	Glass+ITO+ Mesoporous+AL	200℃	YES	Compact absent LowTemperature

Device in reference: in 3.2.3.1

7	Glass+FTO +Mesoporous+AL	500℃	YES	Compact absent

Measuring condition: Pixel 9-10 OVERVIEW

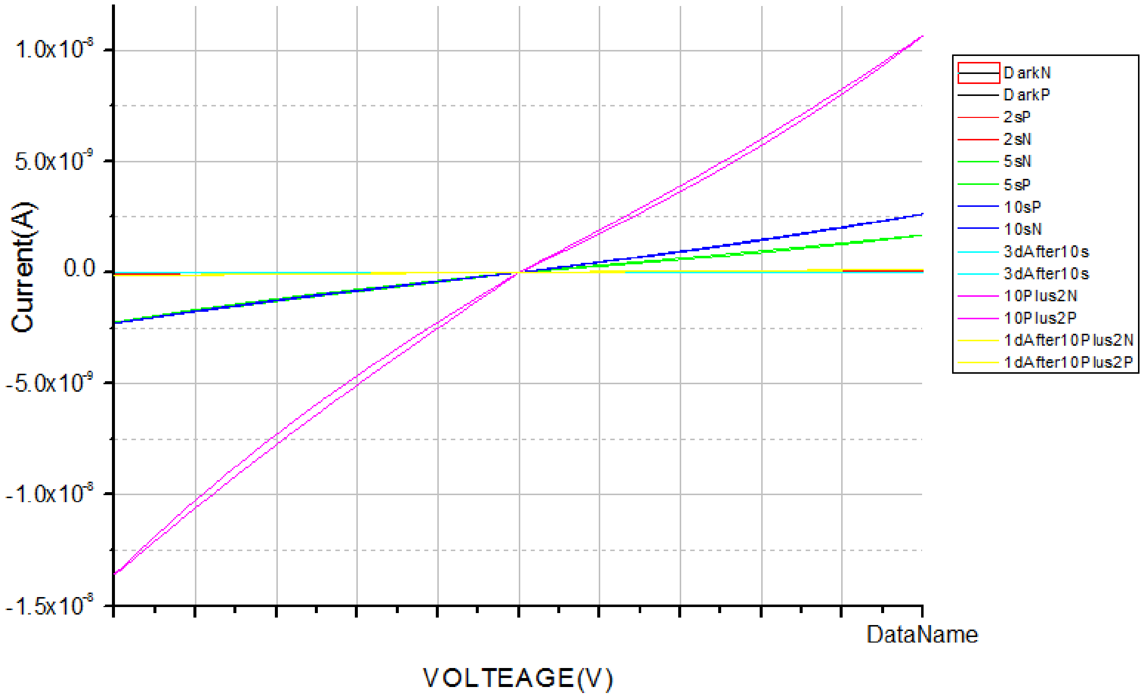

Figure 27. I-V Curve OF Device 4, average pixel 9-10, measured in dark, after 2seconds, 5 seconds, 10 seconds UV Exposure; 3 days after 10 seconds UV exposure; Second UV Exposure with 2 seconds; and 1 day after second UV exposure.

Measuring condition: reversibility check of pixel 9-10.2 second UV light applied again to the device.

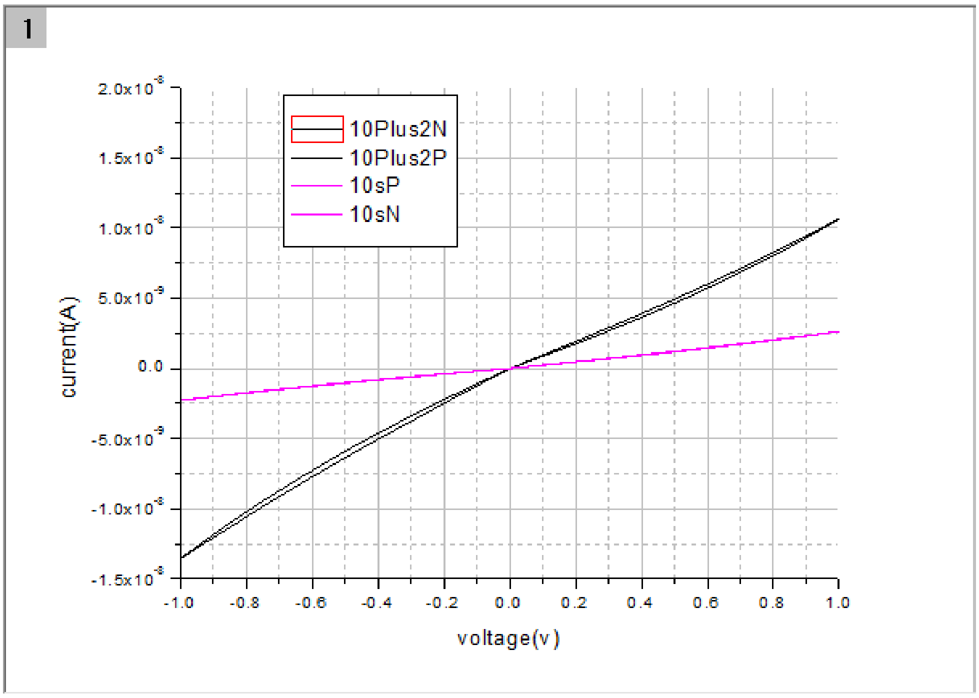

Figure 287. I-V Curve OF Device 4, average pixel 9-10, measured after 10 seconds UV Exposure;; Second UV Exposure with 2 seconds.

Measuring condition: Stability Check of Pixel 9-10.

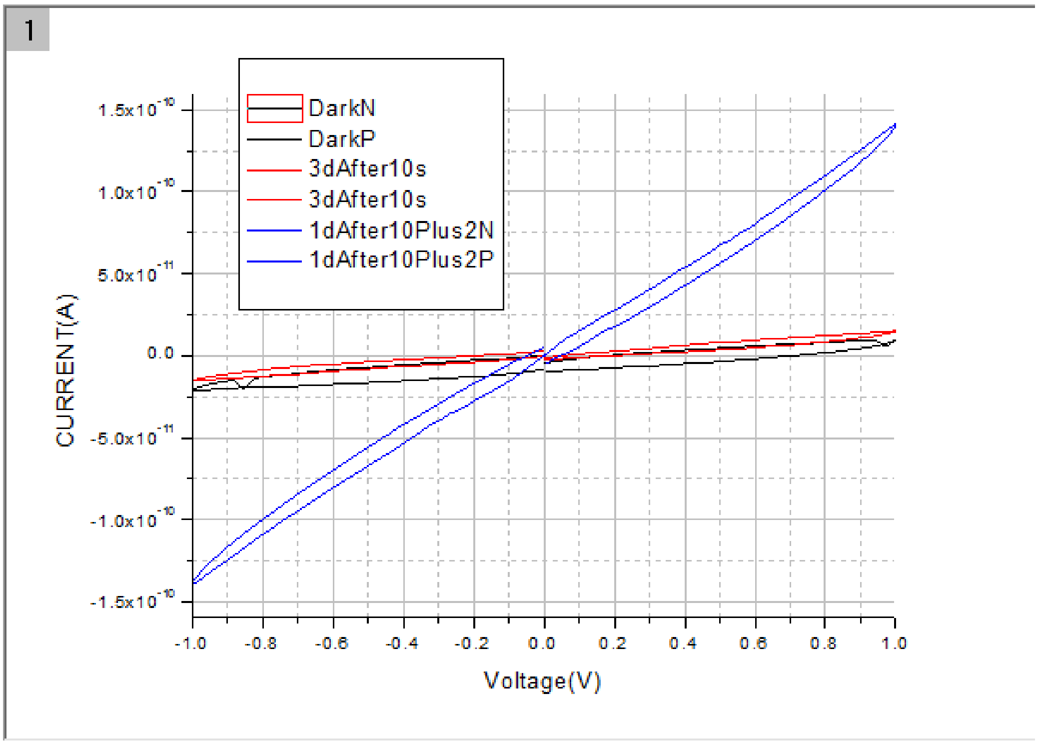

Figure 29. I-V Curve OF Device4, average pixel 9-10, measured in dark; 3 days after 10 seconds UV exposure; 1 day after second UV exposure.

1. The conductivity is starting from 10E-12 to10E-8 after 8s UV light, which is same as in the one without TiCl4 treatment. And it is much lower than device 7 IN 3.2.3.1 case: starting from 10E-2 to 10E-2 after UV light.

2. It is obvious that the device is not stable. After the first UV light, the conductivity reduced until the same order of starting value after 3 days.

3. Pixel 9-10 is the average one in this device. According to its performance, the device may be reversible. We apply 2 second UV light again after the device exposure 10 seconds UV and stay in vacuum for 3 days. The second 2 second UV light increase conductivity to a lager value, then after 1 day, the value stay on 10E-10, which are still 2 orders higher than starting value and it is similar in last case 3.2.4.2.

Comments:

It indicates: The effect of high temperature: vapor the organic part which may reduce the conductivity. We have already see devices cooked in low temperature trends to be poor conductive. It is due to the organic residual during the fabrication process is still inside the device and it have negative effect on the conductivity of material.

At the same time, it helps to confirm:

- without the compact layer the device prone to be short circuit but not sure.

- the relation betweenTiCl4 and stability need more data to support and worth be deeper investigated.

3.3 Organic Residual Observation Measurement

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect.

This shift provides information about vibrational, rotational and other low frequency transitions in molecules and bear the chemical signature of the material under investigation. The spectrum of the Raman-scattered light depends on the molecular constituents present and their state, allowing the spectrum to be used for material identification and analysis.

We used Raman spectroscopy to verify the chemical composition of the photoactive layer in the case of high temperature and low temperature annealed TiO2 mesoporous layer.

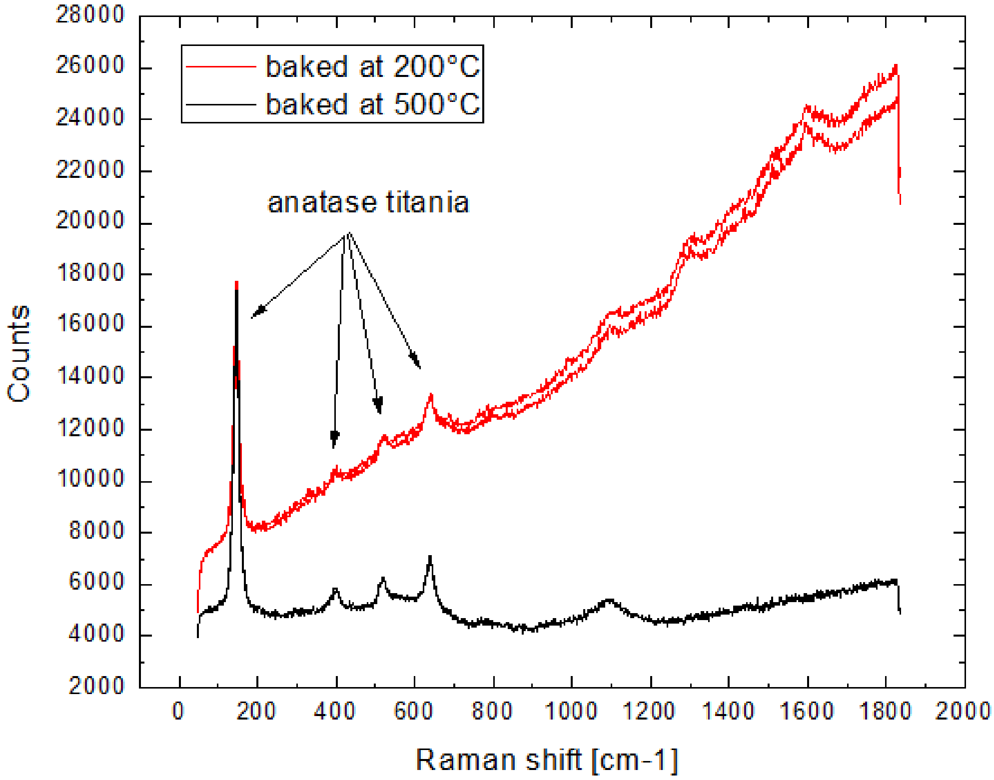

Figure 30. Raman Shift of Low temperature/high temperature devices

The figure confirms the existing of organic residual in the device. The peaks above 1000 are thought to be due to organic residuals, as well as the raising tail in the low temp device (which is due to photoluminescence). The peaks at low Raman shift are characteristic peaks assigned to TiO2 crystalline material.

For depositing the mesoporous layer, we use a commercial Dyesol TiO2 paste which previously diluted in ethanol and ultrasonicated. The paste is made of TiO2 nanoparticles and with organic materials inside to provide solubility. High temperature processing is able to burn the organic ligands and to promote sintering of the nanoparticles together. While in the low temperature devices, lower currents could be due to the presence of organics, but also to the fact that nanoparticles are not well sintered together.

Moreover, in the low temperature device with the TiCl4 treatment, reversibility even in the presence of ticl4 could be attributed to the residual presence of oragnics, which maybe capture and release oxygen upon illumination.

4. Conclusion:

Device	Factor in Consideration	Current Range	Reversible	Note
1	Mesoporous absent	10^{-3}	NOT APPLICABLE	Not work at all, Mesoporous is compulsory
2/8	Compact+TiCl4 absent	10^{-10}=>10^{-3} 10−6=>10−2 10^{-2}=>10^{-2}	YES	Different start conductivity may be due to slightly different thickness of TiO2, To be investigated
3	Compact+TiCl4 absent Low Temprature	10^{-12}=>10^{-8}	YES	Low conductivity due to organic residual
4	Compact absent LowTemperature	10^{-12}=>10^{-8}	YES	Final current have increase on second time UV exposure
5	Same device as reference	10^{-6}=>10^{-2}	NO	Stable in vacuum and dark
6	TiCl4 absent	10^{-6}=>10^{-2}	YES	Stability may related to TiCl4 surface treatment
7	Compact absent	10^{-2}=>10^{-2}	Not Sure	Prone to short circuit

Table 3 Brief Devices Performance Identification

We have identified different behaviors in terms of conductivity, current levels, stability, and reversibility, that we have been able to relate to different device processing and structure.

As for device structure simplification, we have found that mesoporous layer is compulsory for conductive pixel. However is possible to get rid of compact layer if we can find a suitable solution to avoid the short circuit phenomenon.

Suitable device configuration can be chosen based on application.

We have demonstrated working TiO2 pixles based on low temperature processing techniques. Even it have lower conductivity due to organic residual, the general performance is still qualify, with more than a factor 1000 change in conductivity upon few seconds UV illumination

An interesting characteristic we have noticed is the spontaneous slow reversibility of device in vacuum. It implies that the imager can be erased and re-used without change the working condition (vacuum and dark in this case) of the device. This could be a great advantage in application.

At the same time, even if the device is slowly reversible, the information is not destroyed by the reading processHence we can avoid the use of TFT.

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