Electrical characterization of MXenes and their applications on photovoltaic cells

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Abstract: $Ti_3C_2T_x$ is a particular type of MXene whose electrical properties have been studied. Specifically, its performance as a hole transport layer (HTL) in an n-type Si photovoltaic cell has been evaluated and compared to a cell without MXene. Additionally, a layer of a dipolar material, PAMAM, has been implemented alongside with MXene to improve the overall behaviour of the cell. J-V and EQE characteristics have been measured for the different cells and figures of merit have been computed to determine the effect of adding layers of MXene and PAMAM. The measurements have been done at room temperature and after a 100°C annealing. In the end, the obtained results indicate that the behaviour of the cell improves considerably with MXene as a HTL, and even more when the dipoles are present. However, the overall performance of these cells is lacking when compared to modern industrial cells, not making Mxene solar cells an attractive option for commercialization.

Key Words: PV cells, MXenes, selective contact, HTL, dipole, dendrimer, PAMAM.

I. INTRODUCTION

Solar photovoltaic cells are the future of the energy industry. They have become increasingly relevant in the past few years and predictions say that their relevance will continue to grow. Because of this, solar cells must be further researched in order to achieve better efficiencies. Then, the understanding of the operating principle of solar cells is crucial for the comprehension of this project.

In a solar cell, photons from the Sun are used to generate a current and a voltage. Photons reach the semiconductor *absorber region* where, provided they carry enough energy ($h\nu > E_{gap}$), they generate an electron-hole pair. If nothing is done, the net charge through both terminals of the cell would be 0, as electrons and holes would indistinctly cross both terminals or recombine in the absorber. However, by placing a device which blocks holes and allows electrons to pass on one terminal and another device which does the opposite on the other terminal, an intensity is generated. These are known as electron transport layer (ETL) and hole transport layer (HTL) respectively. For an ETL a material with a higher Fermi level than that of the semiconductor is needed, and for an HTL, a lower one.

New materials for the design of more efficient solar cells are constantly being researched upon. In the used cells, MXenes are being put to test. These are a brand new class of 2D inorganic materials with exciting properties.

MXenes are ceramic materials derived from a bulk crystal called MAX and, unlike other ceramics, they have really interesting electrical properties, such as a remarkably good conductivity and an excellent volumetric capacity. Other interesting non-electrical properties are their high hydrophilicity, their large surface area and their relatively high transparency compared to other materials of the same type [1] [2].

Since they can have variable work function [1] depending on the composition, MXenes can work both as a HTL or an ETL [3]. This makes them particularly interesting for the development of solar cells. The MXene being studied in this article is $Ti_3C_2T_x$ (being T_x different terminals which can be either OH, O_2 or F in different quantities). The work function of this MXene is higher than that of the Si substrate. This translates into a lower Fermi level which, when reaching equilibrium, will cause the bands to curve upwards (see figure 2), thus easing the flow of holes into the contact and simultaneously impeding that of electrons, therefore working as a HTL.

Due to its high hydrophilicity, Mxene is kept dissolved in water. Then, in order to create a layer onto the substrate, a drop of this solution is simply deposited on the surface and let dry. However, there is an inconvenience with this procedure as Si is a highly hydrophobic material and the MXene solution is not able to spread correctly on its surface, thus generating important irregularities on the thickness of the layer. One solution to this issue is to add a layer of dipoles in between the MXene and the substrate, improving the permeability.

The application of the dipole layer should also help MXene to be a more efficient HTL due to the orientation of the charges. In our case, the positive charges locate on the side of MXene and the negative charges on the side of Si. This causes a voltage difference between these two layers ($V_{MXene} - V_{Si} > 0$), which makes the vacuum level decrease on the side of MXene, therefore decreasing its Fermi level. This implies that the difference between the Fermi levels of MXene and Si will be even larger, making the bands curve even more. Because of this, holes will find it easier to get out of the absorber region, resulting in a higher HTL efficiency. Among different possible dipoles, PAMAM was chosen for this study.

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[1] The work function of a material ($q\Phi_m$) is defined as the energy difference between its vacuum level (energy of a free electron) and its Fermi level $q\Phi_m = E_{vac} - E_{F_m}$. Thus the higher the work function, the lower the Fermi level, and vice versa.

Poly(aminoamide), or simply PAMAM, is an organic dipolar molecule belonging to a specific group called dendrimers [4]. What makes dendrimers so characteristic is their branched structure. In the process of synthesis of PAMAM, the starting point is the core of the molecule, called initiator, which acts as an active site. After a set of chemical reactions, some radicals are attached to the core, creating generation 0 PAMAM (or G0 PAMAM). These reactions can be done several times, thus creating different generations: G1, G2, G3, etc. The number of branches on each generation grows exponentially, making the size and the dipole moment of the whole molecule increase as well. In theory, the higher the generation, the better the permeability and thus the MXene layer should be more uniform.

In this project several solar cells will be compared, each of them containing MXene and a different generation of PAMAM from G0 to G3. The initial hypothesis is that the overall performance of the solar cell should improve when increasing the generation of PAMAM. There will also be a comparison with two reference cells, one without the PAMAM layer and another without MXene (only Si and ITO).

Before moving on to the experimental part, a brief definition of the figures of merit used to evaluate the performance of the tested solar cells will be made. Photovoltaic efficiency (η) is the ratio between the maximum power produced and incident power (using the AM 1.5G convention of S_{in}=100 mW/cm^2). Current commercial Si cells are above 20% [5]. Another typical figure is the fill factor (FF), the ratio between the maximum power (P_m) and the open circuit voltage (V_{oc}) multiplied by the short circuit current (I_{sc}). This measures the quality of the cell because, as one can see in an I-V characteristic, it depends on how abrupt the change in slope is. For commercial cells, it is around 80% [5].

$$\eta = \frac{P_m}{P_{in}} = \frac{V_m I_m}{S_{in} A} \qquad\qquad FF = \frac{P_m}{V_{oc} I_{sc}}$$

II. STRUCTURE OF THE CELLS

The substrate in which the photons will be absorbed to produce electron-hole pairs is an n-type mono-crystalline Si layer. On top, two thin layers of amorphous Si were deposited, the first intrinsic and the second highly n-doped. On the whole they will act as the electron transport layer (ETL). The top of the cell was then been with an Indium Tin Oxide (ITO) film, effectively working both as an anti-reflection layer and transparent conductive electrode. On the other side, a layer of Mxene acting as a hole transport layer (HTL) was deposited by drop casting. A thin PAMAM layer was applied as well in some of the samples, for the previously explained reasons. Another possible advantage of this structure is that the partial transparency and high conductivity of MXene allows the cells to be bi-facial, making the most out of the light coming from both sides. A final silver film of ∼ 4-5 μm has then been deposited in a grid pattern onto the ITO to provide reduced series resistance with shadow factor of 4%. (See figure 1).

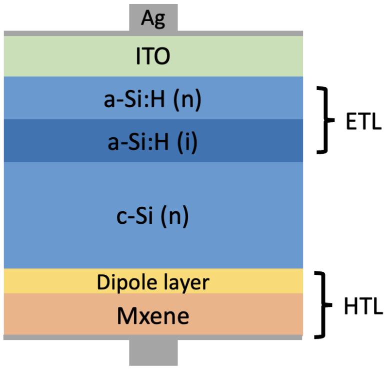

FIG. 1. Layer structure of the tested PV cells.

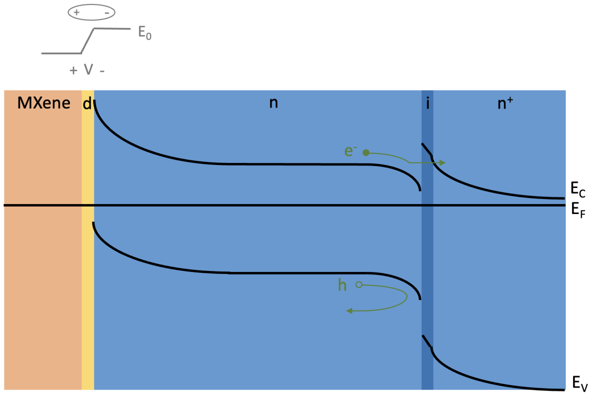

FIG. 2. Band diagram of solar cell in equilibrium.

From now on, each of the cell's behaviour will be studied in different situations, so it is important to define the notation which will be used in the rest of the paper. *Front* will be understood as whenever the top layer, as seen in figure 1 is polarized at a higher voltage (for $V > 0$) than the back and when light is impinging on the top of the cell. *Back* will be the opposite, when the bottom layer is polarized with higher voltage or when light is impinging on the MXene. *Dark* conditions are when no light is illuminating the sample, whereas *light* is when the sample is being illuminated with the AM1.5G spectrum.

III. EQE

One of the most broadly used techniques to measure the performance of solar cells is the External Quantum Efficiency or EQE. The EQE helps quantify the effectiveness of the photovoltaic effect, by impinging monochromatic light on the solar cell and then measuring the ratio of the electrons collected by the solar cells to the incident photons [6]. Ideally, the EQE graphic should be a square across the wavelengths used (determined by the band gap of the material used and the solar spectrum, in our case from 300nm to 1200nm) but, due to various factors, it is typically reduced as seen in the graphs. A reduction in the low wavelengths section is due to front surface recombination and a non-ohmic contact. In the middle region, it is caused by reflection and a low diffusion length[2]. Lastly, a decreasing EQE in the larger wavelengths is attributed to back surface recombination, low energy of the incident photons resulting in a waned absorption and a low diffusion length [7] [8].

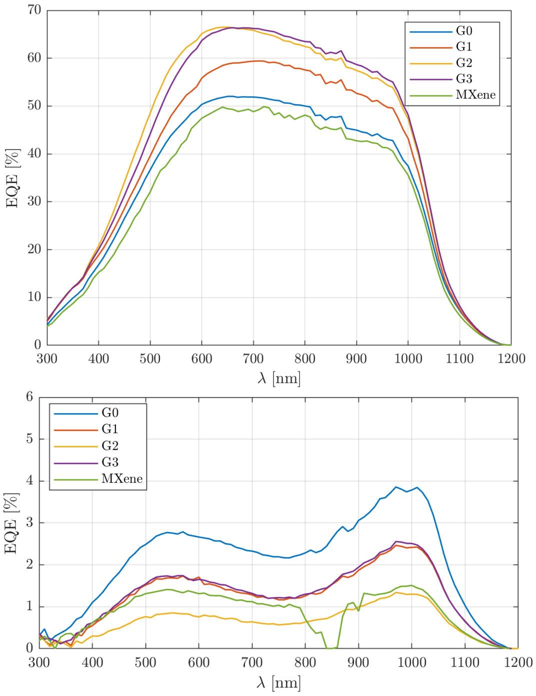

FIG. 3. EQE of the solar cells measuring the front (top) and back (bottom) sides.

One can immediately notice from figure 3 that the EQE on the front side is significantly larger than that of the back side. Moreover, adding the dipole layer not only improves the EQE but also as the molecule of PAMAM grows, that is, as we increase its generation, the efficiency gets better. This is probably because as the dipole moment augments so does the difference in vacuum levels (see figure 2), thus improving the Schottky contact and consequently the HTL character of MXene. Examining the back side graph we conclude that, although it might somewhat contribute, the bi-facial attribute is rather insignificant. The reason for this decay in EQE with respect to the front side is that on the back there is no antireflection treatment and so, although MXene is partially transparent, it still prevents for a considerable amount of photons to enter the cell. Furthermore, it does not seem to order in generations of PAMAM nor we get a sense of improvement from the only MXene cell when compared with those that do have a dipole layer.

IV. I-V CHARACTERISTIC

In order to evaluate the performance of a solar cell, the shape of the intensity-voltage curve (I-V) is crucial. To obtain this, a voltage source sweeps from -1V to 1V while an ammeter measures the current. Since the current is proportional to the area of the device, the results will be given in terms of current per unit area (J) to facilitate the comparison with other cells.

It can be shown that the response in current of a solar cell to an applied voltage while being illuminated by light is the superposition of the J-V response under dark conditions with the response to the light applied when short-circuited. The first is identical to the response of a diode to an applied voltage. The second is a negative current proportional to the intensity of the light.

$$J = J_{dark}(V) - J_{sc} = J_0(e^{V/V_T} - 1) - J_{sc}$$

Following the definitions imposed by consensus of intensity I and voltage V in a circuital device, power is consumed when $P = IV > 0$ and is generated when $P = IV < 0$. In an I-V characteristic, this occurs when the curve belongs to the second or fourth quadrants. Given that the purpose of a solar cell is to generate power and that the previous function will never be in the second quadrant, the curve of a good solar cell must be in the fourth quadrant until the maximum possible value of V (V_{oc}). This is why, when designing a solar cell, one aims to obtain a large V_{oc} and J_{sc}, which will generate the largest possible power.

In a semi-logarithmic plot, a good cell will have the dip in intensity as far right as possible, maximizing V_{oc}, and the current at $V = 0$, J_{sc}, will be also maximum. As seen in figure 4 for front polarization, adding MXene as a HTL improves V_{oc} and J_{sc} considerably. Then, the PAMAM layer helps improve J_{sc}. There is also an improvement for back measurements but not nearly as good, which falls in line with the results of the EQE. Furthermore, the quality of the diodes can also be studied. Neither the front nor back measurements show much resemblance to an ideal diode, which would be linear for large V, but the back ones are linear for longer than the front, indicating smaller parasitic resistances.

Additionally, by processing the data from the experiment, the mentioned figures of merit can be obtained and are summarized in table I and table II, with the exception of J_{sc} which is taken from the EQE, as the lamp used for this measurement was properly calibrated to the AM1.5G spectrum. For the complete data, see supplementary information (S.I and S.II).

Firstly, as anticipated from the EQE and as foreseen in the semi-logarithmic plots, the back efficiency η is very

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[2] The diffusion length is the average distance a carrier (electron or hole) moves before recombining, so, in a solar cell, a high enough diffusion length is key for the carrier to reach its respective selective contact and therefore produce a current.

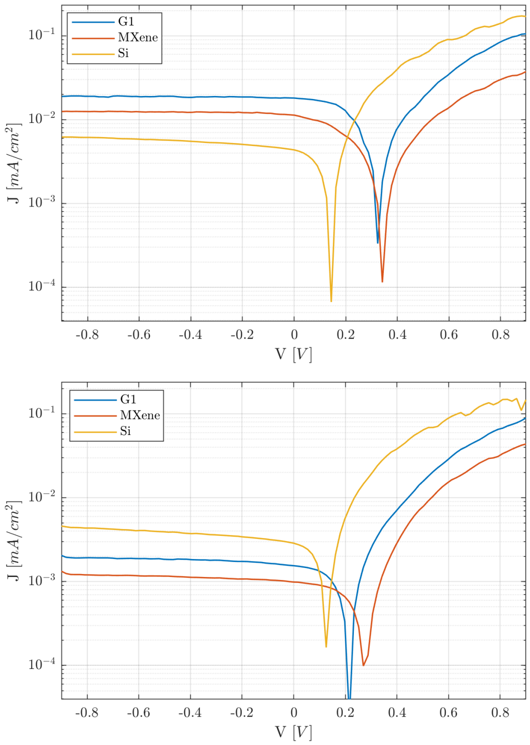

FIG. 4. Comparison of the J(V) characteristic of the different cells in front light (top) and back light (bottom) polarizations.

low in all cases. For front polarization, the efficiencies are higher, but still not very good compared to regular Si cells. As expected, the MXene reference cell performs better than the Si cell, and the presence of PAMAM dipoles further improves the efficiency. We see that in general, as we could predict with the EQE, η and FF get better as we increment the generation of the dendrimers.

FRONT	$\mathbf{V_{oc}}$[V]	$\mathbf{J_{sc}}[\frac{\text{mA}}{\text{cm}^2}]$	$\mathbf{P_m}[\frac{\text{mW}}{\text{cm}^2}]$	**FF**[%]	η[%]
G0	0.3489	17.94	222.642	35.57	2.2264
G1	0.3268	20.32	292.053	43.98	2.9205
G2	0.3447	22.86	270.909	34.38	2.7091
G3	0.3617	22.69	336.076	40.95	3.3608
Si	0.143	10.04	68.5413	47.74	0.6854
MXene	0.3444	16.77	195.1571	33.79	1.9516

TABLE I. Figures of merit for the front side in light.

BACK	$\mathbf{V_{oc}}$[V]	$\mathbf{J_{sc}}[\frac{\text{mA}}{\text{cm}^2}]$	$\mathbf{P_m}[\frac{\text{mW}}{\text{cm}^2}]$	**FF**[%]	η[%]
G0	0.2686	1.10	14.927	50.52	0.1493
G1	0.2148	0.65	6.893	49.37	0.0689
G2	0.2701	0.33	4.5324	50.85	0.0453
G3	0.2946	0.67	9.9698	50.51	0.0997
Si	0.1288	0.91	4.9532	42.26	0.0495
MXene	0.2777	0.45	6.1408	49.14	0.0614

TABLE II. Figures of merit for the back side in light.

Finally, the samples underwent annealing at 100°C with the idea of increasing their performance. This process generally improves the figures of merit of semiconductor devices [9] [10], so it was reasonable to assume the same would be true for these samples. However, the results obtained cannot be accurate, since the lamp with which the curves were measured was not calibrated, and unfortunately, it was not possible to do another EQE with the annealed samples.

Still, a qualitative conclusion can be drawn by comparing J_{sc} at room temperature (RT) and at 100°C. This is done in figure 5 for G2 (and for all PAMAM in supplement S.I & S.II), where it can be seen that V_{oc} decreases but an increase in J_{sc} makes up for it, ultimately netting an increase in P_m, FF and η.

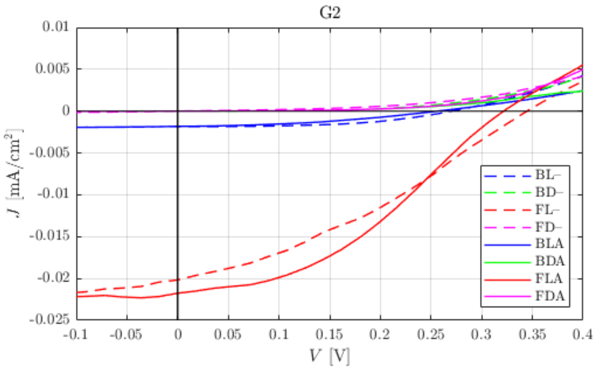

FIG. 5. J-V characteristic of the cell with G2 PAMAM for both polarizations, front (F) or back (B), in light (L) or dark (D) conditions, at RT (–) and with annealing at 100°C (A).

V. CONCLUSIONS

This study has demonstrated that MXene does work as HTL and that adding a dipole layer improves the efficiency. This parameter also grows with each generation of PAMAM, probably because of the increased dipolar moment. The efficiency of the cells is low, which may be due to the oxidation of the MXene. Given not much additional performance is gained from making them bifacial, adding a metallic layer on the back, for instance Ag, to prevent oxidation could prove beneficial. Alternatively, an antireflectant layer could have been added for better performance.

Moreover, after seeing the improvement with annealing, another one at higher temperatures could be an interesting follow-up study to this one. It would be crucial, however, that the temperatures were not too high due to the organic nature of the PAMAM dipoles.

After taking into account all of this, it has been concluded that these PV cells are not competitive enough to be commercialized, as current commercial cells have significantly better performance. However, another focus can be given to these devices, as due to their good photo-response they may be used, for instance, as photodetectors. Either way, further research is still needed.

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