NiO Thin Films Deposited by Reactive HiPIMS: From Plasma Diagnostics to Improvement of the Solar Cells Efficiency

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ABSTRACT

In this paper we establish the link between the plasma, the properties of the deposited thin films by reactive HIPIMS and the solar cells efficiency. In the first part we have demonstrated that it is easy to transfer from DC to HiPIMS discharge conditions using discharge voltage measurements and optical emission spectroscopy (OES) at different amount of reactive gas. The transition between metallic and poisoned mode is clearly identified in both cases. The second part is dedicated to the characterization of NiO thin films. In DC case, the structure is always columnar and in HiPIMS case the structure is dense and very well crystallized. By photoelectron spectroscopy (XPS) and energy dispersive spectrometry (EDS), we have found that stoichiometric films are obtained at the beginning of the fully oxidation mode. Finally, we present the characterization of solar cells synthesized with our films, and we conclude to the improvement of these cells using NiO, deposited by HiPIMS, as anode buffer layer (ABL). The lifetime of these cells is 17 times higher and the efficiency about 2.5 times higher than cells without NiO as ABL.

INTRODUCTION

To obtain the best possible results, the plasma must be carefully controlled. Unfortunately, because plasma processes suffer from drift, process recipes that initially produced optimal results may no longer produce acceptable results at later times [1]. This problem has been solved using plasma diagnostics. Despite the large number of research on thin films, there are only a few studies in HIPIMS (High Power Impulse Magnetron Sputtering) plasma diagnostics [2]. In this paper we attempt to establish the link between the plasma, the properties of the deposited thin films by reactive HIPIMS and the solar cells efficiency. In the first part we demonstrate that it is easy to transfer from DC to HiPIMS discharge conditions using discharge voltage measurements and optical emission spectroscopy (OES) at different amount of reactive gas. The second part is dedicated to the characterization of NiO thin films. In DC or HiPIMS, the average power is fixed at 100W, the pressure at 0.66 Pa, the working gas is Argon (10 sccm) + O_2 (0 to 5 sccm), the cathode-substrate distance: 4 cm and the substrate is at a floating potential. For HIPIMS, the pulse width is 30 μs and the frequency 1 kHz (duty cycle = 3 %). The peak power is about 4 kW. We present the influence of the percentage of reactive gas on the morphology and structure of thin films and we compare to DC case. The techniques used are photoelectron spectroscopy (XPS), energy dispersive spectrometry (EDS), the X-ray diffraction (XRD), scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM). Finally, we present the characterization of solar cells synthesized with our films, and we conclude to the improvement of these cells using NiO, deposited by HiPIMS, as anode buffer layer (ABL).

PLASMA DIAGNOSTIC

In other studies we have investigated the NiO properties deposited by DC reactive magnetron sputtering [3, 4]. It has been shown that the oxygen content is the main parameter to manage morphology, the preferential crystallographic orientation and the electrical properties. With relatively low oxygen content, the films show an increase in the (111) diffraction peak related to the standard JCPDS card (No: 89-7130); and rich oxygen content films were characterized by the predominance of the (200) peak intensity. For electrical conductivity, it has been highlighted that before the transition, the films are metallic; in the transition zone, the films are close to intrinsic semi-conductor (low conductivity) and after the transition, the conductivity increase due to the presence of Ni^{3+} in the crystal cell. In this part we attempt to use plasma diagnostic (discharge voltage and Optical Emission Spectrometry) in order to transfer from DC to HiPIMS the best discharge conditions obtained in DC case.

The first step is the electrical characteristic of the discharge as a function of the oxygen/argon. This diagnostic is an easy handling technique giving fast updated information (potentially less than a few milliseconds). The signal strongly depends on the oxidized level of the cathode surface [5]. In DC case we have differentiated 3 regimes, on the characteristic of discharge voltage (Figure 1a).

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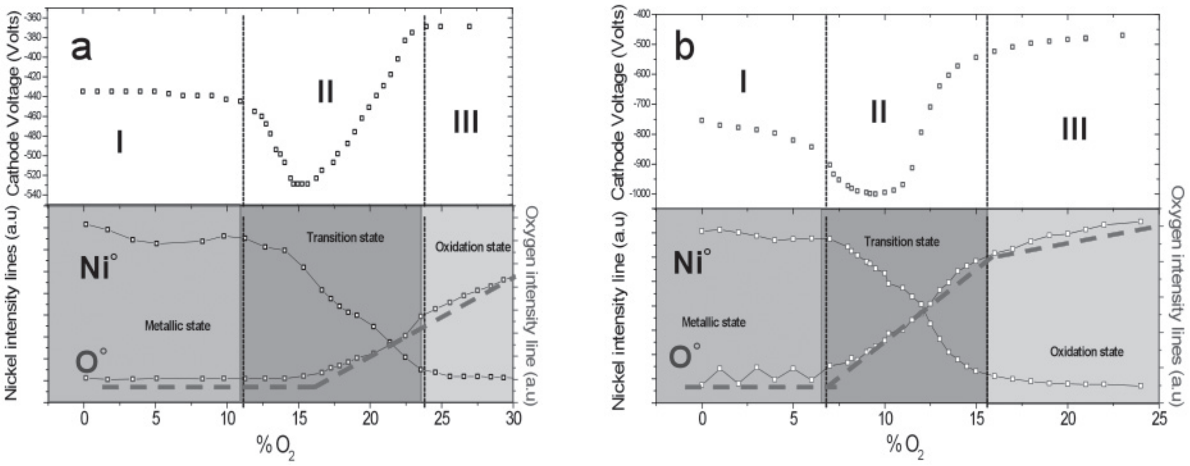

Figure 1: Discharge voltage and optical emission of DC (a) and HiPIMS (b) plasma as a function of oxygen content.

The first region correspond to the metallic state, the oxygen species reaching the target are removed by the ion bombardment, allowing the target to remain metallic and therefore the discharge voltage does not change significantly. The second region, where the films are more or less transparent, corresponds to the transition state. First, the amount of oxygen reaching the target starts to become higher than the oxygen removed by sputtering. The target potential increases (absolute value) due to the increase of secondary electron emission coefficient and reaches a maximum value corresponding of the formation of NiO layer on the target surface and the creation of negative oxygen ions [6, 7]. These negative ions consume electrons, and are not trapped by the magnetic field, hence in order to maintain the discharge current, the cathode voltage increases. The third region correspond to the so-called poisoned mode (fully oxidized state), the discharge voltage stabilized again at a lower (absolute value) discharge voltage. For optical emission measurements we have followed the integrated lines intensities of Ni^0 and O^0 lines at respectively at 351.5 and 777.4 nm. The decrease of the Ni^0 lines and the increase of the O^0 line correspond exactly to the creation of negative oxygen ions described earlier.

We have done the same experiment in HiPIMS case (Figure 1b), and we have found the same behavior for the discharge voltage as a function of oxygen content. The OES measurements show also the same behavior for the Ni^0 line. For the O^0 line, the increase differs, it begins earlier probably due to an improvement of the electron impact dissociation of the oxygen molecule.

This part of work is very interesting in the sense that it is very easy to transfer the DC optimized deposition conditions, to HiPIMS ones, using basic plasma diagnostics. Moreover, the films have the specific HiPIMS properties such as a high density and a high crystallinity level.

THIN FILMS CHARACTERIZATIONS

All the thin films have been characterized by EDS and XPS (Figures 2a and b). For EDS, the voltage acceleration used was 5 kV, which corresponds to 200 nm depth analyses. For XPS, prior to analysis, the films were eroded with argon ions (Energy fixed at 500 eV) and the pass energy was fixed to 20 eV.

In both cases (DC and HiPIMS) the O/(Ni+O) ratio increases linearly and is equal to 50 % (stoichiometric films) when the discharge voltage reaches the maximum value: 15 % for DC

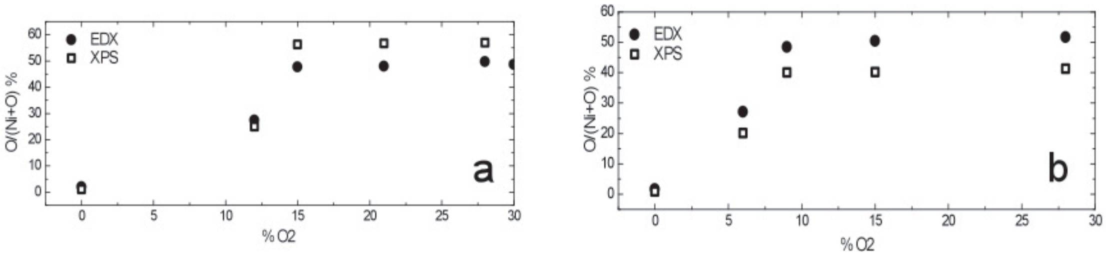

Figure 2: EDS and XPS characterization of NiO thin films deposited by DC(a) and HiPIMS (b) as a function of oxygen content.

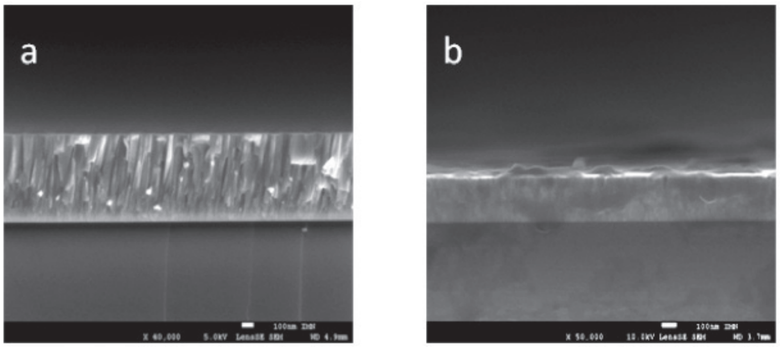

Figure 3: Cross section SEM images of NiO with 28% amount of oxygen deposited by DC (a) and HiPIMS (b).

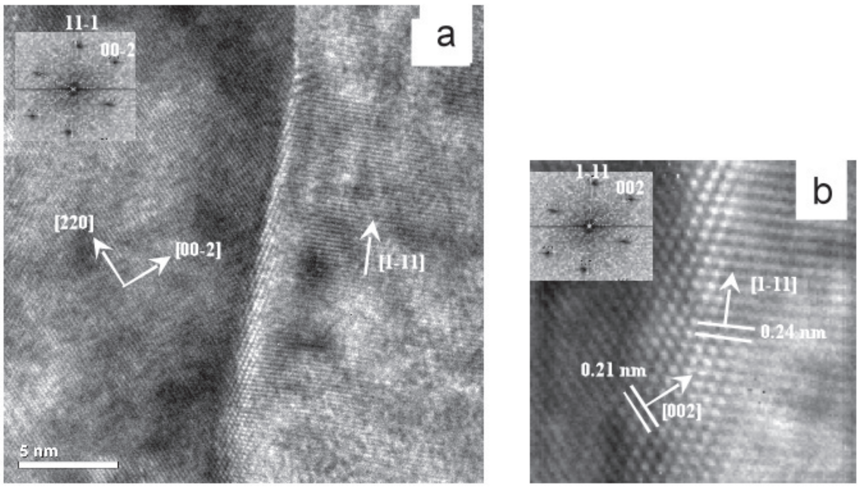

Figure 4: High resolution TEM image of NiO thin-film deposited on Si (100) substrate showing the grain boundary between NiO crystals, viewed along [1-10] (left) and [110] (right). Insets: respective FFT and filtered high resolution image.

and 10 % for HiPIMS. After these values, increasing oxygen content in the discharge, leads to nickel deficient films which are clearly p-type with a resistivity in the range of 1 Ω.cm [8]. In HiPIMS case, the oxygen present at the extreme surface (XPS) is lower than in DC case, it is probably due to denser films without columnar structure and to well crystallized grain boundaries as shown on SEM and HRTEM pictures (Figures 3 and 4).

APPLICATIONS TO ORGANIC SOLAR CELLS

It is well known that ITO is very sensitive to acidic environments. The hygroscopic nature of CuPc allows the absorption of water from the ambient environment, which facilitates the etching of the ITO layer, giving rise to degradation and deterioration of the device stability [9]. In this study, the organic solar cells used were based on the classical junction copper phthalocyanine (CuPc)/fullerene (C60). CuPc is the electron donor and C60 the electron acceptor. Aluminum Alq3 has been used as exciton blocking layer (EBL) because it allows the lifetime of the OPVs. The optimized thicknesses were 35 nm for CuPc, 40 nm for C60 and 9 nm for Alq_3 [10]. The NiO has been used as anode buffer layer (ABL). The cells were typically: glass/ITO/NiO/CuPc/C60/Alq_3/Al (Figure 5).

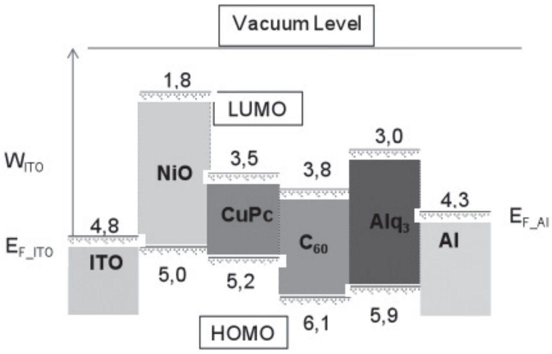

Figure 5: Energy diagram and materials used in our OPVs.

In Table 1 it can be seen that there is an improvement of the OPVs performances when the thickness of NiO films increase from 10 to 20 nm. 20 nm is the optimal thickness whatever the sputtering process (DC or HiPIMS) [11].

Table 1: OPVs performances with NiO ABL.

Thickness (nm)	V_{oc} (mV)	J_{sc} (mA/ cm^2)	FF (%)	h (%)	R_s (W)	R_p (W)
10	355	5.3	37	0.7	4.7	105
15	430	5.2	59	1.3	6.6	1030
20	439	6.5	60	1.7	9	907
25	439	5.7	47	1.2	8	232
30	428	4.4	57	1.1	3.6	1060

Figure 6 shows the lifetime results performed in the dark under ambient air, a temperature of 20-23°C and 50-55 % relative humidity. The structure is very unstable without ABL and the PCE and JSC have been strongly reduced after one hour of storage. However, the efficiency of the PVO cell based on ABL NiO decreases only by 3 % in one hour, meaning that lifetime is higher than 17 times and the efficiency about 2.5 times that of ITO/CuPc/C60. This study confirmed that the interface ITO/NiO improve the OPVs efficiency and stabilized strongly the structure.

CONCLUSION

In this paper we have demonstrated that it is easy to transfer from DC to HiPIMS discharge conditions using discharge voltage measurements and optical emission spectroscopy. For the films, in DC case, the structure is always columnar and in HiPIMS case the structure is dense and very well crystallized. We have found that stoichiometric films are obtained at the beginning of the fully oxidation mode. Finally, using NiO deposited by HiPIMS as ABL in OPVs, improvement the lifetime of these cells (17 times higher) and the efficiency (about 2.5 times higher).

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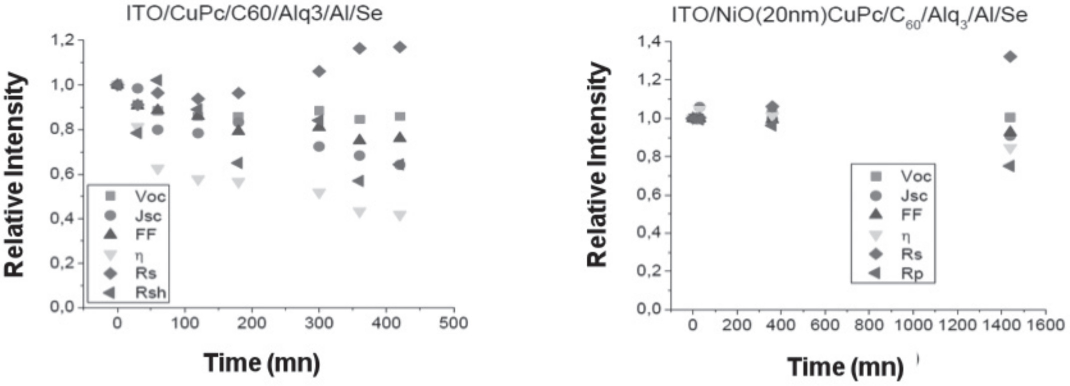

Figure 6: OPVs lifetime without (left) and with (right) NiO as ABL.