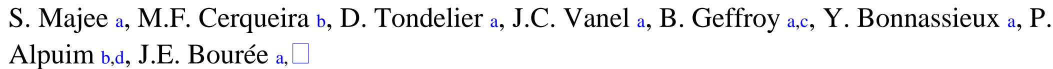
Permeation barrier performance of Hot Wire-CVD grown silicon-nitride films treated by argon plasma



S. Majee [a], M.F. Cerqueira [b], D. Tondelier [a], J.C. Vanel [a], B. Geffroy [a,c], Y. Bonnassieux [a], P. Alpuim [b,d], J.E. Bourée [a,]

[a] Laboratoire de Physique des Interfaces et des Couches Minces, CNRS UMR 7647, Ecole polytechnique, 91128 Palaiseau, France
[b] Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal
[c] Laboratoire de Chimie des Surfaces et Interfaces, IRAMIS/SPCSI CEA Saclay, 91191 Gif-sur-Yvette, France
[d] INL–International Iberian Nanotechnology Laboratory, 4715-330 Braga, Portugal

ABSTRACT

In this work we produce and study SiNx thin films deposited by Hot-Wire Chemical Vapor Deposition (HW-CVD) technique to be used as encapsulation barriers for flexible organic electronic devices fabricated on polyethylene terephthalate (PET) substrates in order to increase their shelf lifetime. We report the results of SiNx multilayers stacked and stacks of SiNx single-layers (50 nm each) separated by an Ar-plasma surface treatment. We assess the encapsulation barrier properties of these different multilayers, using the calcium degradation test by monitoring changes in the electrical conductance of encapsulated Ca sensors with time. The water vapor transmission rate is found to be slightlyminimized (7×10^{-3} g/m^2day) for SiNx layers exposed to argon plasma treatment during a short time (2 min) compared to that for SiNx stacked single-layers without Ar plasma treatment.

INTRODUCTION

Organic light emitting diodes (OLEDs) and organic solar cells fabricated on flexible polymer substrates are rapidly emerging devices because they offer many advantages compared to conventional LEDs and silicon solar cells, namely low cost, light weight, flexibility and thereby roll to roll process-ability. However, the organic devices are very sensitive to moisture and oxygen which limits considerably their shelf lifetime.

The encapsulation of such devices is considered as a critical issue to be solved in order to enable their long termstability and deployment. Instead of glass as an encapsulation protection, more and more attention has been paid to the development of high-quality inorganic films or alternating organic and inorganic films due to their flexibility and
their high barrier performance [1,2].

For the commercial use of plastic-based (PET) organic devices, there is a wide range of permeation requirements for different materials and applications. The widely quoted requirement for water vapour transmission rate (WVTR) for an OLED with a lifetime of N10,000 h is 10^{-6} $g/m^2 \cdot$day [3]. Some recent studies demonstrate that the encapsulation of organic photovoltaic cellswith barrier materials corresponding to a WVTR in the range between 10^{-4} and 10^{-3} $g/m^2 \cdot$day is sufficient to achieve lifetimes of several thousands of hours in operation [2,4,5].

The main characteristics required for the permeation barrier films are their high density, defect-freeness, good adhesion, thermal stability and uniform thickness. Moreover, high electrical resistivity, high transparency, and stress freeness are needed for these films as well as the ability to be deposited at low temperature in order to be compatible with the use of plastic substrates [6].

The objective of this work has been to study the barrier properties of SiNx single-layer films deposited by HW-CVD, either piled up one after the other or piled up with an argon plasma surface treatment (during a fixed time) between two successive single-layers. Compared to plasma enhanced chemical vapor deposition (PE-CVD),HW-CVD allows low substrate damage due to the absence of ion bombardment, low hydrogen content of the deposited material and finally conformal step coverage [7–11]. HW-CVD also allows low deposition temperature which is compatible with the use of polymer substrates. The idea behind the use of argon plasma surface treatment is to rearrange locally the first atomic layers near each interface in order to make the diffusion of water vapour molecules through the multilayers stacked more difficult [12]. This rearrangement should increase the effective time for these molecules to diffuse throughout the barrier layer toward the organic device surface. We assess the WVTR values for SiNx thin-film multilayers stacked on PET substrates, with and without argon plasma surface treatments and compare these values with WVTR values assessed for uncoated PET substrates.

EXPERIMENTAL DETAILS

Sequences of SiNx single-layers (named as A samples) and sequences of SiNx single-layers, each layer being separated from the next one by Ar plasma surface treatment (named as B samples) are obtained using the HW-CVD process. For the B samples, the Ar-plasma treatment is realized in a glow discharge chamber, where the sample is clamped to the top electrode and heated to the treatment temperature, and the bottom electrode is the rf-powered electrode.
We first reached the optimal growth conditions for the SiNx single layers, namely leading to high transparency (T N 80%), films with high density and good dielectric properties (refractive index, n of ~2 at 632.8 nm). Both procedures (growth and plasma treatments) are performed at a fixed substrate temperature of 100 °C in order to be compatible with the use of PET substrates. The substrate temperature is measured with a thermocouple embedded in a stainless steel substrate-holder, close to the substrate. This means that, especially for the depositions made nominally at 100 °C, the temperature of the film growing surface is certainly higher than the substrate-holder temperature due to the heating from the hot filament [13]. Whenever the substrate temperature read at the Eurotherm display exceeds the nominal deposition temperature by 10% (110 °C), the deposition is stopped. Thus the single-layer thickness is limited to 50 nm which corresponds to a growth time of 360 s. Then we realized multilayer stacks of SiNx filmswhere the number of 50 nm thick single-layers varied from 1 to 5.
In order to reach the optimal growth conditions for the SiNx films we fixed the working pressure at 25 mTorr and changed three parameters: the hydrogen dilution [flow rate of hydrogen / (flow rate of hydrogen + flow rate of ammonia + flow rate of silane)], the R ratio (flow rate of ammonia / flow rate of silane) and the Ta filament current, Ifil. The flow rates of hydrogen and silane have been fixed at 54 sccm and 2 sccm respectively.
The Ar plasma surface treatment is performed at 50 mTorr working pressure during a short time (2 min) in the rf (13.56 MHz) PECVD reactor. The power density is fixed at 350 mW/cm2. The sequence of SiNx deposition and Ar treatment is performed without breaking the vacuum. This is achieved by moving the sample between two twin chambers connected by a gate valve.
Our aim is to achieve smoothed layers on PET substrates. The average surface roughness of the SiNx single-layers as well as single-layers separated by Ar plasma surface treatment is measured using atomic force microscopy (AFM) technique.
To measure thewater vapor transmission rate (WVTR) valuewe use the electrical calcium degradation test [14–16] method implemented inside a glove box flushed with permanent nitrogen with less than 0.1 ppm of oxygen and water vapor. For the Ca degradation test, 100 nmCa layerwith an area of 1.13 cm2 and aluminumcontacts are deposited by thermal evaporation through shadow masks on the back side of the barrier coated PET substrates. The barrier coated substrates are degassed at 90 °C for about 6 h inside the glove-box prior to the Ca deposition. A low deposition rate of 0.2 nm/s (measured by using a calibrated quartz crystal microbalance near the substrate) and at a pressure of aprox. 10−6 mbar is chosen to get a really smooth layer for both calcium and aluminum deposition. The Ca layer plus part of the Al contacts are then covered with a glass plate. All of these parts are sealed with epoxy resin (Nagase Chemtex Corp. XNR 5570), which is cured under UV-lamp (365 nm wavelength) inside the glove-box. In order to check the sealing quality, the calcium test is also performed on a glass substrate (glass-glass sample). Therefore, the Ca layer is deposited on one side of the barrier film and the other side is exposed to the environment (see Fig. 1). The calcium degradation test is performed under ambient environmental condition. Water molecules in the environmental moisture after diffusing through the pinholes and defects inside the barrier, reach the calcium sensor and react with the sensor and thus reduce its conductivity. The change of conductance is measured using a four point probe technique of Solartron-Schlumberger 7060 Systems Voltmeter. The permeation rate or WVTR is evaluated fromthe average slope of the evolution of the conductance of calcium sensor.

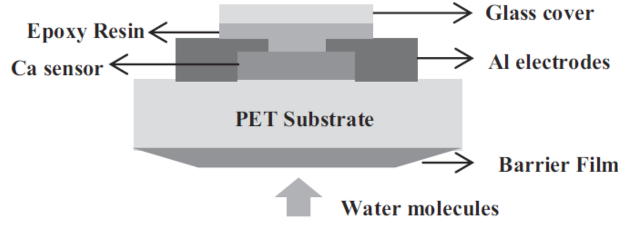


Fig. 1. Schematic side view of electrical calcium degradation test setup (dimensions are not to the scale).

RESULTS AND DISCUSSION

SiNx films were optimized for their optical transmittance, refractive index and deposition rate, in this order. We targeted highly transparent films in the visible region (transmittance N 80%) which are simultaneously dense (n ~ 2) and obtainable at a deposition rate, rd, as high as possible. Highly transparent films are required for window layers in photovoltaic cells. A refractive index of 2 means that the SiNx films are dense and close to stoichiometry (as opposed to porous films which have lower n, and Si-rich films which have higher n but are not fully transparent). A high rd is important for economical reasons in general and in this case it also allows avoiding long exposure of the plastic substrate to the hot filament.

Fig. 2 shows optical transmission spectra of as-deposited single layers (A samples) and single-layers with Ar plasma surface treatment (B samples), acquired in the wavelength range from 250 to 750 nm. All the samples reveal a transmittance above 60% for wavelengths larger than 500 nm. We verify that, in general, the transmittance increases with the Ar treatment (Fig. 2). The film thickness and the spectral refractive index, n, are obtained from the transmission spectra in the visible range applying the Minkov method [17] and adopting a classical Lorentz/Drude dielectric function for the dispersion behavior of the dielectric constant.

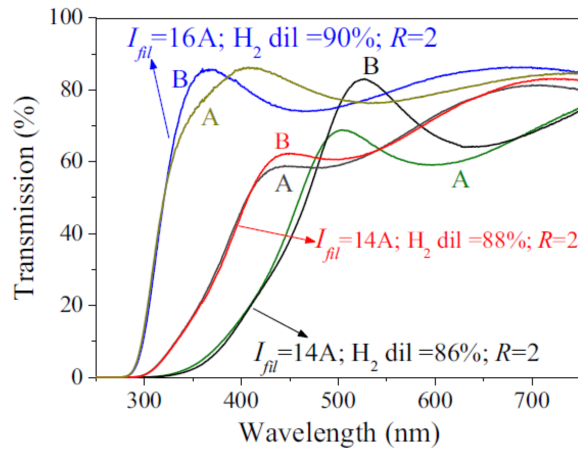


Fig. 2. Transmission spectra of some 250 nm thick SiNx samples. "A" curves represent the untreated SiNx samples and "B" curves represent the Ar plasma treated samples.

Fig. 3(a) shows the refractive index of the SiNx single-layers as a function of ammonia-to-silane gas flow rate ratio (R), for differentH2 dilutions and filament currents (Ifil).Most of the films have n N_2 which is attributed to a Si-rich composition. The refractive index approaches the stoichiometric value of 2 when R is increased from 2 to 3, when Ifil increases from 14 to 16 A, or when H2 dilution increases from 86% (88% at R = 3) to 90%, keeping fixed all the other parameters.

Fig. 3(b) shows the effect of varying the same parameters that were varied in (a) on rd. The information contained in the figure can be summarized by noting that rd increases, as expected, when Ifil increases from 14 to 16 A, and decreases when H2 dilution increases from 86% (88% at R=3) to 90%, or when R increases from 2 to 3. The effect of H2 dilution on rd is explained by

the surface etching of defective film tissue by atomic hydrogen while the R-effect is mainly due to the increase in gaseous fraction of the reactant gas (NH3) with higher atomic bond energy.

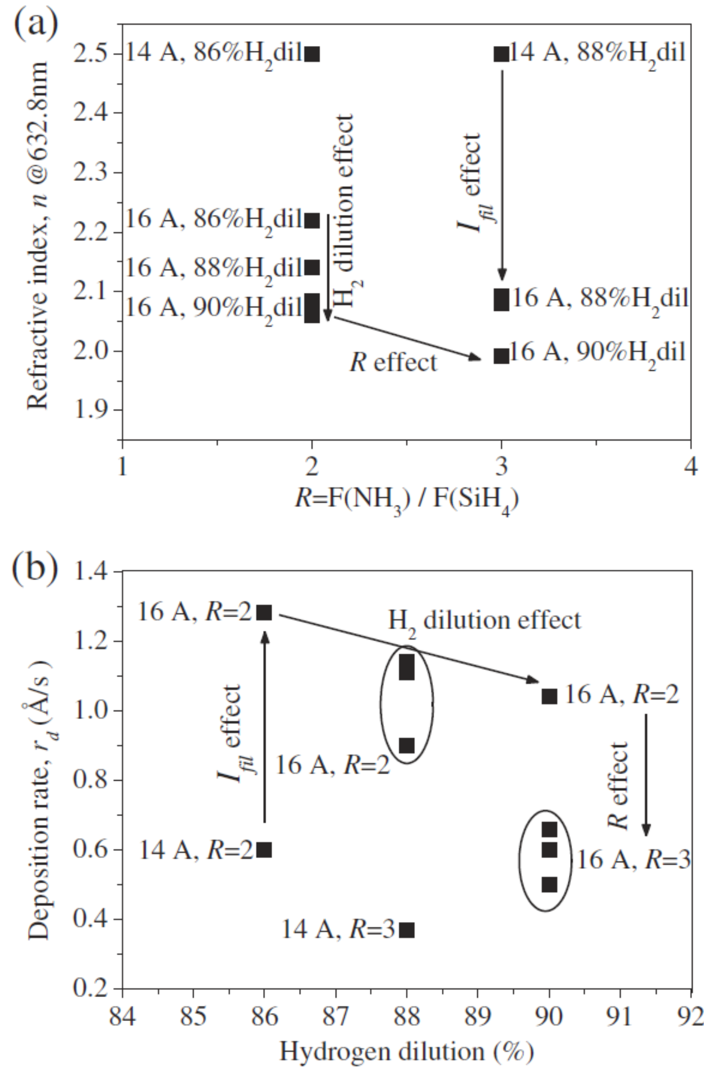


Fig. 3. (a) Refractive index, n and (b) deposition rate, rd for the different single-layers of SiNx, as a functionof filament current (Ifil), NH3 and SiH4 gas flowrate ratio (R) and hydrogen dilution.

Taking into consideration all the above results (Figs. 2, 3(a) and (b)), single (50 nm) andmultilayers (number of layers × 50 nm) of SiNx thin films are obtained using the optimized conditions, namely 90% hydrogen dilution of silane and ammonia gaseous mixtures; Ta filament current of 16 A, corresponding to a filament temperature of 2000 °C, and relative flowrates of NH3 and SiH4 (R) of 2,which give films with visible transmittance higher than 80%, n ~2 at 632.8 nm and rd = 1.4 Å/s. We note here that compared to our previous work [18], the substrate-to filament distance is now increased to 7.5 cm, in order to avoid excessive heating of the PET substrates which have a maximumworking temperature of ~110 °C. Under these conditions we found that lowering the working pressure from 40 mTorr to 25 mTorr and using H2 dilution of the reactant gases yield more dense and transparent films than could be obtained by using the optimized deposition parameters for the conditions described in [18].

Fig. 4 shows the average sample roughness, obtained by atomic force microscopy of the SiNx single and multilayers and single and multilayers separated by Ar-plasma surface treatment. It should be noted that the average roughness of the bare PET substrate after exposure to the hot filament for the same time (360 s) as it takes for one single layer deposition, but without film

growth, is 55 nm. The initial average roughness for PET foils before being exposed to HW-CVD process is 1.35 nm. The roughness of PET increases strongly when the PET foil is exposed to the Ta filament, probably due to the fact that the glass transition of PET starts at around 80 °C. It is clear from Fig. 4 that all the SiNx layers, in the range of thickness studied, have the effect of reducing the roughness of the bare substrate from 55 nm to 15.5 nm and 26 nm for the untreated and Ar-treated films, respectively. The lowest average surface roughness of 15.5 nm is achieved for the sample with 5 layers × 50 nm/layer = 250 nm without Ar-plasma surface treatment.

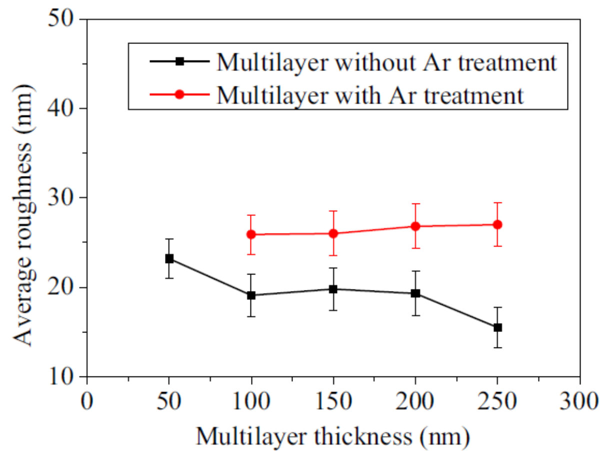


Fig. 4. Average surface roughness (by AFM) as a function of layer thickness for SiN_x samples with and without Ar plasma treatment.

Fig. 5 shows the cross sectional SEM image of the interface between 250 nm thick SiNx multilayer deposited without argon plasma surface treatment and the PET substrate. This micrograph shows some 100 nm wide cracks passing through the film. These cracks ease the permeation of the water molecules through the film and could be the reason for a possible device failure fabricated on such barrier coated PET substrates. But due to the action of the argon plasma surface treatment, the path of the water molecules is expected to become torturous and longer and thus decreasing the WVTR value.

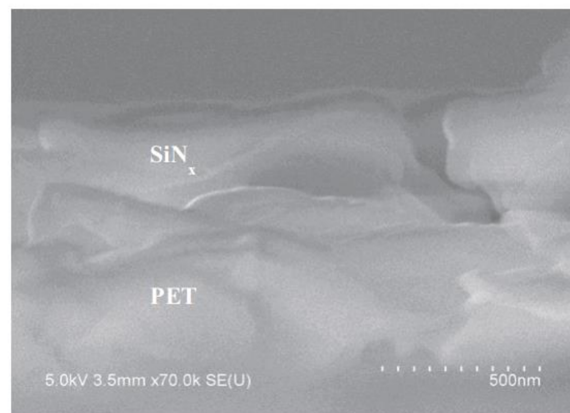


Fig. 5. Cross sectional image of untreated 250 nm thick SiN_x multilayer on PET substrate showing the presence of cracks crossing through the film.

Fig. 6 shows the evolution of normalized conductance of Ca sensor, deposited on uncoated PET and barrier coated PET substrates. The evolution of normalized conductance of glass–glass sample is also shown for comparison. It is confirmed that the water permeation through the epoxy edge-seal is negligible. The WVTR value is deduced from the average slope of the evolution of conductance (dG/dt) using the following relation [14,16]:

$$WVRT\left[{}^{g}/_{day.m^2}\right] = -N\delta_{Ca}\rho_{Ca}\frac{M(H_2O)}{M_{Ca}}\frac{l}{w}\frac{d(G)}{dt}\frac{area(Ca)}{area(window)}$$

where N is the molar equivalent of the degradation reaction which is assumed as N = 2 from the chemical reaction of Ca with water [Ca + 2H2O → Ca(OH)2 + H2], M is the molar mass of the reactive elements, δCa is the density of calcium (1.55 g/cm3), ρCa is the calcium resistivity (9 × 10^{-8} Ω·m which is in good agreement with ref. [14]), l and w are the effective length and width of Ca layer respectively and G is the conductance. From the geometry of our setup, the value of Area (Ca) / Area (window) is taken to be unity.

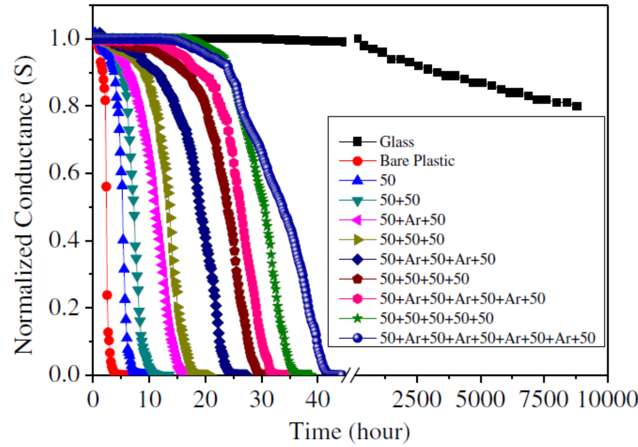


Fig. 6. Normalized conductance of Ca sensors deposited on bare PET as well as on barrier coated PET substrates vs time. Normalized conductance of Ca deposited on glass is used as reference.

The degradation test is performed on 10 uncoated PET substrates (Melinex ST 504, 175 μm thick) to evaluate the reproducibility of the measurement. The WVTR value assessed from the conductance evolution curve shows that the uncoated PET substrate has a WVTR of 0.17 ± 0.05 g/m2·day, whereas the glass substrate shows an estimated WVTR of ~10−6 g/m2·day to prove the limit of our test set-up (based on the results of 8000 h of evolution, shown in Fig. 6). The evolution of WVTR values as a function of thickness of barrier is shown in Fig. 7, which reveals the effect on permeation values by increasing the number of SiNx single-layers. For the 50 nm SiNx layer deposited on PET substrates, the water vapor transmission rate decreases to 1.3×10^{-2} g/m^2·day as compared to the bare PET substrate. With further increase of thickness, the WVTR value goes down and the lowest value found for 5 SiNx single-layers stacked is 7.9 $\times 10^{-3}$ g/m^2·day. With the argon plasma surface treatment, there is slight decrease in the WVTR value which goes down to 7×10^{-3} g/m^2·day for the 5 SiNx single-layers, each separated by Ar plasma surface treatment. These results confirm that the permeation rate decreases with the number of single-layers and also with the Ar plasma surface treatment, even with a short treatment time (2 min). Future research direction can concern the study of argon plasma surface treatment parameters to reduce the permeation rate further.

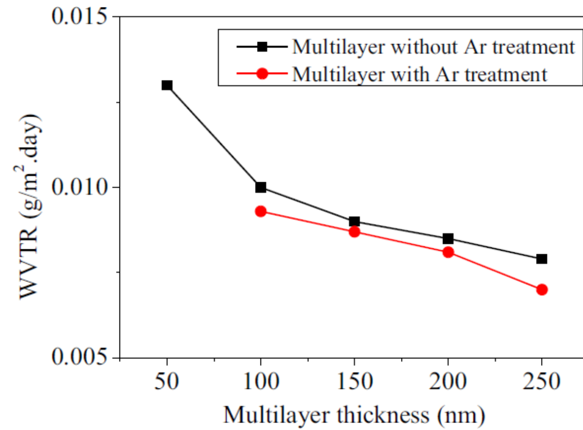


Fig. 7. Variation ofWVTR values versus the thickness of the SiN_x films with and without Ar plasma treatment.

CONCLUSION

Using the HW-CVD technique, and after an optimization taking into account the different growth parameters we have deposited device quality SiNx films to be used as barrier layers for flexible organic electronics, using silane and ammonia gaseous mixtures diluted in hydrogen at Tsub = 100 °C. Using the electrical calcium degradation test, we have demonstrated the decrease of WVTR value for PET covered with SiNx layers compared to bare PET substrates. Furthermore, we have shown that Ar plasma surface treatment (during a short time) between successive SiNx single-layers further reduces the WVTR value down to 7×10^{-3} g/m^2·day.

ACKNOWLEDGMENTS

The authors would like to thank Cyril Jadaud for his help inmechanical design, Jacqueline Tran, Bicher Haj Ibrahim and Martin Foldyna for optical characterization techniques used in this study. The first author (S.M) acknowledges the financial support from Direction des Relations Extérieures, Ecole polytechnique during his thesis. This study has been supported by PICS (French-Portuguese project no. 5336).

References

[1] D. Spee, K. van der Werf, J. Rath, R. Schropp, Phys. Status Solidi (RRL) 6 (2012) 151.
[2] H. Nakayama, M. Ito, Thin Solid Films 519 (2011) 4483.
[3] P.E. Burrows, G.L. Graff, M.E. Gross, P.M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, L. Michalski, M. Weaver, J.J. Brown, D. Fogarty, L.S. Sapochak, Proc. SPIE 4105 (2001) 75.
[4] J.A. Hauch, P. Schilinsky, S.A. Choulis, S. Rajoelson, C.J. Brabec, Appl. Phys. Lett. 93 (2008) 103306.
[5] S. Cros, R. de Bettignies, S. Berson, S. Bailly, P. Maisse, N. Lemaitre, S. Guillerez, Sol. Energy Mater. Sol. Cells 95 (2011) S65.
[6] J. Fahlteich, M. Fahland, W. Schonberger, N. Schiller, Thin Solid Films 517 (2009) 3075.
[7] Y. Ogawa, K. Ohdaira, T. Oyaidu, H. Matsumura, Thin Solid Films 516 (2008) 611.
[8] H. Matsumura, J. Appl. Phys. 66 (1989) 3612.
[9] H. Matsumura, H. Umemoto, A. Izumi, A. Masuda, Thin Solid Films 430 (2003) 7.
[10] A. Masuda, M. Totsuka, T. Oku, R. Hattori, H. Matsumura, Vacuum 74 (2004) 525.
[11] A. Heya, T. Niki, Y. Yonezawa, T. Minamikawa, S. Muroi, A. Izumi, A. Masuda, H. Umemoto, H. Matsumura, Jpn. J. Appl. Phys. 43 (2004) 1362.
[12] J. Ubrig, S. Martin, S. Cros, J.E. Bourée, J. Phys. Conf. Ser. 100 (2008) 082030.
[13] J.E. Bourée, S.R. Jadkar, S. Kasouit, R. Vanderhaghen, Thin Solid Films 501 (2006) 133.

[14] R. Paetzold, A. Winnacker, D. Henseler, V. Cesari, K. Heuser, Rev. Sci. Instrum. 74 (2003) 5147.
[15] S. Schubert, H. Klumbies, L. Muller- Meskamp, K. Leo, Rev. Sci. Instrum. 82 (2011) 094101.
[16] M.O. Reese, A.A. Dameron, M.D. Kempe, Rev. Sci. Instrum. 82 (2011) 085101.
[17] D.A. Minkov, J. Phys. D. Appl. Phys. 22 (1989) 199.
[18] P. Alpuim, L.M. Gonçalves, E.S.Marins, T.M.R. Viseu, S. Ferdov, J.E. Bourée, Thin Solid Films 517 (2009) 3503.