Effects of a ZnO buffer layer on the resistivity and transmittance of GZO/AZO multilayer films deposited by r. f. magnetron sputtering on polymer substrates

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Al-doped ZnO (AZO), Ga-doped ZnO (GZO), and GZO/AZO thin films were deposited on polymer (PET) substrates with and without a ZnO buffer layer by using an r.f. magnetron sputtering technique and their structural, electrical, and optical properties were investigated to develop transparent conductors for flexible display applications. The transparent conducting oxide (TCO) films with a ZnO buffer layer showed better electrical and optical properties than those without a buffer layer. The crystal quality of the former was better than the latter, the electrical resistivity of the former is lower than the latter, and the transmittance of the former was also as high as that of the latter. The optimum buffer layer thickness with which the lowest resistivity of GZO/AZO/ZnO films was obtained was found to be 150μm. On the other hand it was found that there was little difference in electrical, and optical properties between AZO, GZO and GZO/AZO films with a ZnO buffer layer.

Key words: Ga-doped ZnO, Al-doped ZnO, transparent conducting oxide, r.f. magnetron sputtering, buffer layer

1. Introduction

Transparent conducting oxides (TCOs) are used in optoelectronic devices such as flat panel displays and solar cells. Indium tin oxide (ITO) has been widely used as a TCO since it has visible transmittance, low electrical resistivity and relatively high work function [1]. Nevertheless, ITO is an expensive TCO since indium in ITO is a rare and expensive element. Therefore, impurity-doped zinc oxide (ZnO) has been actively investigated as an alternative to ITO. Impurity-doped ZnO is more favorable than ITO particularly because it is cheaper, easier to etch and more resistant to hydrogen plasma reduction and can be grown at lower temperatures. Group IIIA elements such as Al, In, Ga, and B have been widely used as n-type dopants for ZnO [2-4].

Recently the necessity of studying deposition of TCO films on polymer substrates has increased because polymer substrates are suitable for flexible displays and electronics the demands of which are expected to increase explosively in the near future. Polymers have merits that they are cheaper and lighter than glass, but they also have several demerits. In comparison with glass substrates, polymer substrates have a lower thermal resistance, a weaker mechanical strength and a higher thermal expansion coefficient $(20 \times 10^{-6}$ /K)[5]. The difference in thermal coefficient between polymer substrates and ZnO films $(4.75 \times 10^{-6}$ /K [6]) may result in residual thermal stress-induced defects. Other shortcomings of polymers as substrate materials for TCO are that they easily absorb moisture and gas [7]. Therefore, it is necessary to use a buffer layer when TCO films are deposited on polymer substrates which will make the polymer substrate surface smoother and reduce diffusion of vapor and oxygen. In this work the electrical resistivity and transmittance properties were investigated for Ga-doped ZnO(GZO), Al-doped ZnO(AZO) and GZO/AZO thin films deposited on polyethylene terephalate (PET) substrates with ZnO buffer layers by using an r.f. magnetron sputtering technique.

2. Experimental

GZO and AZO thin films were deposited on PET substrates by r.f. magnetron sputtering using a 2 inch GZO (Ga_2O_3 : 3 wt%, ZnO : 97 wt%) and AZO (Al_2O_3 : 3 wt%, ZnO : 97 wt%) target. The PET substrate surfaces were cleaned in an ultrasonic cleaner for 10 min with isopropyl alcohol and then blown dry with nitrogen before they were introduced into the sputtering system. Prior to the deposition of GZO and AZO thin films ZnO buffer layers were deposited using a 2 inch ZnO target. A ZnO buffer layer is expected to reduce the damage which would be done on the PET surface during deposition of the GZO and AZO films without using a buffer layer and to prevent chemical reaction with oxygen and moisture in air and their diffusion into the PET substrate. The details of the process parameters for GZO and AZO thin films are presented in Table 1. A gas mixture of Ar and O_2 (The flow rates of Ar and O_2 are 10 and 20 sccm, respectively.) were blown into the sputter chamber for 30 min to reduce the damage by ion bombardment during the sputtering process and to decrease the electrical resistivity of the GZO and AZO films [8].

For the prepared samples the carrier concentration, the carrier mobility, and the resistivity were determined by using a Hall effect measuring system (HEM-2000). X-ray diffraction (XRD: Rigaku 2500 PC) was performed to

investigate the crystallinity of the GZO and AZO films. The full width at half maximum (FWHM) of the ZnO (002) XRD peak was measured from the XRD diffraction pattern to assess the crystallinity. The surface morphologies of the GZO and AZO films were investigated by scanning electron microscopic analysis. An α-step (Dektak-3) was used to measure the thicknesses and the surface roughness of the films. The optical transmittance measurements were made by using an UV/VIS spectrophotometer.

Table 1. The standard r.f. magnetron sputtering process parameters for GZO, AZO and ZnO thin films deposition

	ZnO	GZO	AZO
r.f. power (W)	80		
Process pressure (Torr)	5×10^{-3}		
Base pressure (Torr)	1×10^{-7}		
Subs. temp.($^\circ$C)	RT		
Dist. (cm)	8		
Ar/O$_2$ gas flow ratio	20 : 10	30 : 0	

3. Results and Discussion

Figure 1 shows the carrier concentration, the carrier mobility and the electrical resistivity of the GZO/AZO/ZnO films deposited on PET substrates with or without a ZnO buffer layer as a fuction of the buffer
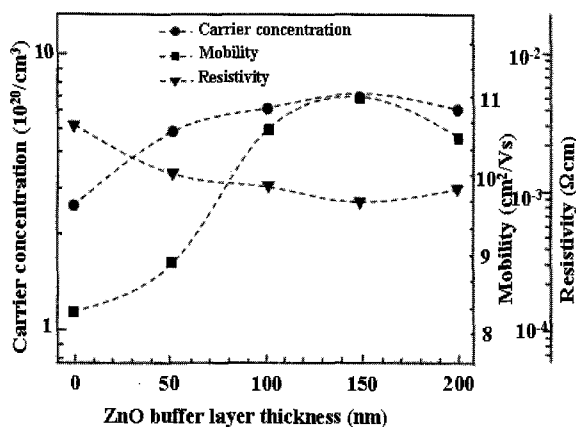

Fig. 1 The carrier concentration, the carrier mobility, and the resistivity of the GZO/AZO films deposited on the PET substrate with and without a ZnO buffer layer. The GZO/AZO films were deposited by R.F. magnetron sputtering with an R.F. power of 80 W and an Ar gas flow rate of 30 sccm

layer thickness. Each of the GZO and AZO film thickness measured by using an α-step was about 200 nm. The resistivity of the GZO/AZO/ZnO films prepared on the PET substrate by using magnetro sputtering in this work is in a range from 3×10^{-3} to $9 \times 10^{-4} \Omega$ cm. This resistivity value is somewhat higher than the minimum resistivity values of impurity-doped ZnO such as AZO and GZO

deposited by sputtering on the glass substrate, but it is relatively lower in comparison with the resistivities of AZO and GZO films deposited on plastic substrates. The minimum resistivities of AZO and GZO films on glass substrates obtained by others are in a range from 1×10^{-4} to $5 \times 10^{-4} \Omega$ cm[9] and those of AZO and GZO on plastic substrates fall in a range from 1×10^{-2} to $5 \times 10^{-4} \Omega$ cm[10] depending on the preparation technique, deposition process parameters and whether a buffer layer was used. On the other hand, it is know that the resistivities of ITO films are somewhat lower than those of impurity-doped ZnO films. It is not so simple to say a minimum resistivity of an ITO film because it depends on many parameters, but it seems reasonable to state that a minimum resistivity of the ITO film is in the region of low $10^{-4} \Omega$ cm. The minimum resistivity values of ITO in references are $1.8 \times 10^{-4} \Omega$ cm[11] on polymer and $2.0 \times 10{-}4 \Omega$ cm on glass[12]. The resistivity of the GZO/AZO/ZnO/PET sample decreases as the buffer layer thickness increases up to 150 nm and then the resistivity increases with continued increases in the buffer layer thickness. In other words, a minimum resistivity is obtained by using a buffer layer 150 nm thick. A decrease of the resistivity in a buffer layer thickness range below 150 nm is attributed to the enhancement of the crystallinity of the GZO/AZO films and an increase in the grain size of the GZO/AZO film. XRD patterns for the GZO/AZO thin films deposited at room temperature on PET substrates with ZnO buffer layers of different thicknesses are shown in Fig. 2.
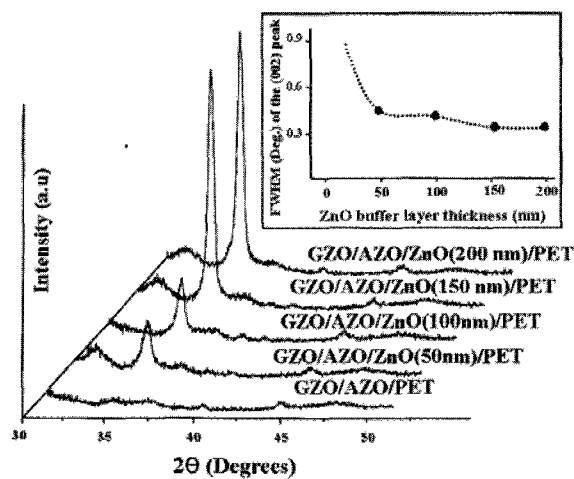

Fig. 2 X-ray diffraction patterns and the FWHM of the (002) peak for the GZO/AZO thin films deposited on the PET substrate with and without a ZnO buffer layer.

An (002) peak appearing at a 2θ of ~ 34.1° indicates that the GZO/AZO films were grown with a c-axis orientation. The (002) peak height increases rapidly and the FWHM decreases as the buffer layer thickness is increased. These changes in the (002) peak height and FHWM confirm us that the GZO/AZO films quality has been improved by using the ZnO buffer layer. As can be seen from the above discussion, there is no doubt that the electrical properties of the GZO/AZO films are enhanced by using a ZnO buffer layer. However, these electrical and optical properties of the GZO/AZO/ZnO/PET sample are still inferior to those of the GZO/AZO/glass sample. This

inferiority is attributed to the weak intrinsic properties of the polymer (PET) such as low thermal stability, low mechanical strength, high thermal expansion coefficient and easy absorption of gas and moisture in the air. On the other hand, an increase in the resistivity of the GZO/AZO/ZnO/PET sample in a buffer layer thickness range above 150 nm is attributed to an increase in the thickness of the ZnO buffer layer which has a higher resistivity than the GZO and AZO films. If the ZnO buffer layer thickness increases above a certain level, a resistivity-increasing effect due to the higher resistivity of ZnO becomes larger than a resistivity-decreasing effect due to an enhancement of the crystallinity of the GZO and AZO films and an increase in the average grain size of the GZO and AZO films.

Figure 3 tells us that the surface roughness of the GZO/AZO films can be decreased by using a buffer layer but it tends to increase as the buffer layer thickness is increased beyond a certain level. The ZnO buffer layer
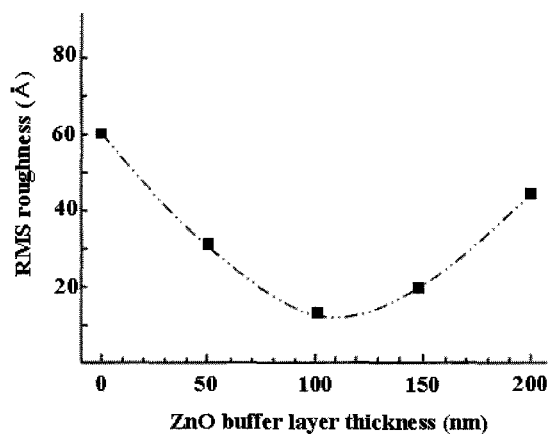

Fig. 3 Dependence of the GZO/AZO film surface roughness on the thickness of the ZnO buffer layer for the GZO/AZO/ZnO/PET samples.
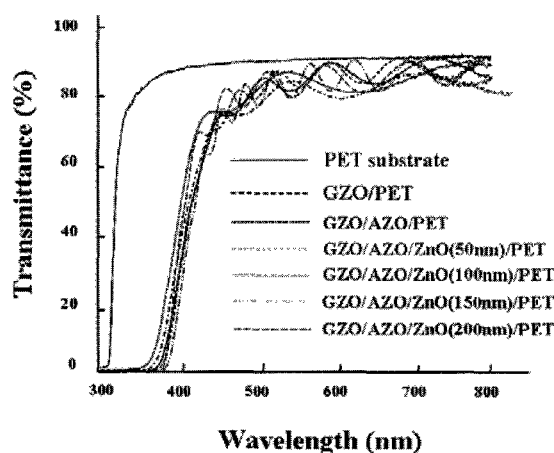

Wavelength (nm)

Fig. 4 The optical transmittance of the GZO/AZO/ZnO/PET samples in the wavelength range from 300 to 800 nm.

thickness for a minimum surface roughness does not coincide with that for minimum resistivity, which suggests that the resitivity of the GZO/AZO/ZnO/PET sample is

less affected by surface roughness than other factors such as crystallinity and grain size.

The optical transmittance spectra of the GZO/AZO/ZnO/PET samples in the wavelength range from 300 to 800 nm are shown in Fig. 4. The transmittance spectra of the PET substrate and the GZO films are also shown for the purpose of comparison and they have optical transmittance higher than 90 and 85% respectively. The overall transmittance of GZO/AZO/ZnO/PET is almost the same as GZO/AZO/PET. The transmittance of the GZO/AZO/ZnO/PET sample seems to be nearly independent of the buffer layer thickness. The GZO/AZO films with a ZnO buffer layer have higher transmittance in the red region but lower transmittance in the blue region. This dependence of the transmittance of the GZO/ZnO/PET samples on the wavelength can be explained with etalon interference effect, which can be inferred by changing colour for different view angles [8].

Table 2 shows the carrier concentrations, mobilities and resistivities of GZO and AZO films with or without a ZnO buffer layer along with a GZO/AZO film with a ZnO buffer layer. It is evident that films with a ZnO buffer layer have lower resistivities than those without the buffer layer. The lower resistivities of the films with a buffer layer must be attributed to the buffer layer. As written in "Introduction", a buffer layer makes the polymer substrate surface smoother and reduces diffusion of vapor and oxygen. Therefore, the TCO films with the ZnO buffer layer have lower densities of impurities and crystallographic defects.

The XRD spectra in Fig. 5 clearly show that the films with the ZnO buffer layer have far lower full width at half maximum (FWHM) values and far higher (002) diffraction peak, which suggests that the crystallinity of a TCO film is substantially improved by using a buffer layer. The improvement in the crystallinity of the TCO film makes positive effects on both components of the resistivity, i.e. increases both the carrier concentration and mobility. There is no doubt that introduction of a buffer layer is essential in depositing TCO films on polymer.

Figure 6 shows that the surface roughness of a TCO film is also improved by using a ZnO buffer layer. The RMS surface roughness values of the GZO and AZO films decreased by 30 – 40 % owing to the buffer layer. It is natural that the improvement in the surface roughness of the TCO film increases the carrier mobility by reducing and thus decreases the resistivity of the films surface scattering. Consequently, the resistivity was decreased by using the buffer layer. The resistivity of the GZO film without a ZnO buffer layer is slightly higher than that of the AZO film without a ZnO buffer layer. In contrast, the resistivity of the GZO films with a buffer layer is slightly higher than that of the AZO film with a buffer layer. The resistivity of the AZO film is reduced more than that of the GZO film by using a ZnO buffer layer. However, the difference is not significant enough to be regarded as the one solely due to the introduction of the buffer layer or the difference in the TCO material. Also the experimental results in Table 2 tells us that it is not advantageous from the viewpoint of electrical properties to use a multilayer TCO film such as GZO/AZO/ZnO.

Table 2. A comparison of the electrical properties of GZO, AZO and GZO/AZO films deposited on PET substrates by sputtering with and without a ZnO buffer layer.

Sample	Carrier concentration n (cm^{-3})	Carrier mobility μ (cm^2/Vs)	Resistivity ρ (Ω cm)
GZO(350*)/PET	3.1×10^{20}	8.5	2.4×10^{-3}
AZO(350)/PET	2.7×10^{20}	8.0	2.9×10^{-3}
GZO(200)/ZnO(150)/PET	7.3×10^{20}	9.0	9.5×10^{-4}
AZO(200)/ZnO(150)/ PET	7.0×10^{20}	10.0	8.9×10^{-4}
GZO(100)/AZO(100)/ZnO(150)/PET	7.1×10^{20}	9.3	9.5×10^{-4}

* The film thickness in nm

Fig. 6 A comparison of the surface roughness of the GZO, AZO, and GZO/AZO films with and without a ZnO buffer layer.
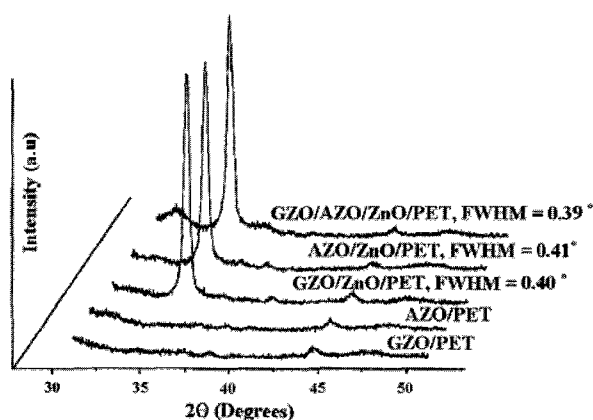

Fig. 5 X-ray diffraction patterns and the FWHM of the (002) peak for the GZO,AZO and ZnO thin films deposited on the PET substrate with and without a ZnO buffer layer.

Fig. 7. The optical transmittance of the AZO/ZnO/PET samples in the w avelength range form 300 to 800 nm.

This decrease in the surface roughness is attributed to the reduction in lattice mismatch between the TCO film and the polymer substrate by introducing the ZnO buffer layer. The buffer layer seems to do its duty of reducing diffusion of vapor and oxygen and making the TCO film surface smoother.

An envelope method using the maxima (T_{max}) and minima (T_{min}) of transmittance of optical films measured at a spectrophotometer is a simple method to determine the optical constants (refractive index and extinction coefficient) and the thickness of weakly absorbing thin films [13]. In the case of optical thin-films with a higher refractive index than that of substrate, T_{min} and T_{max} correspond to the quarter- and half-wave optical thicknesses of thin films, respectively. Further, if the optical films are non-absorbing, T_{max} at the half-wave optical thicknesses of films should touch the transmittance of substrate.
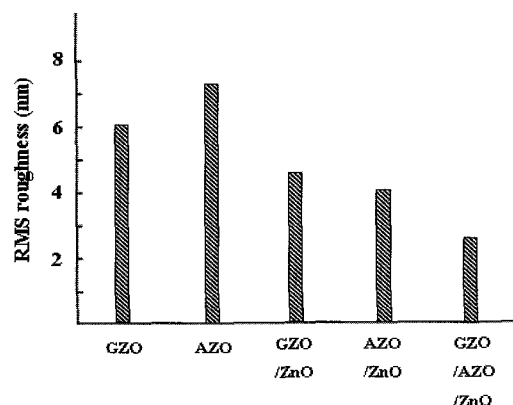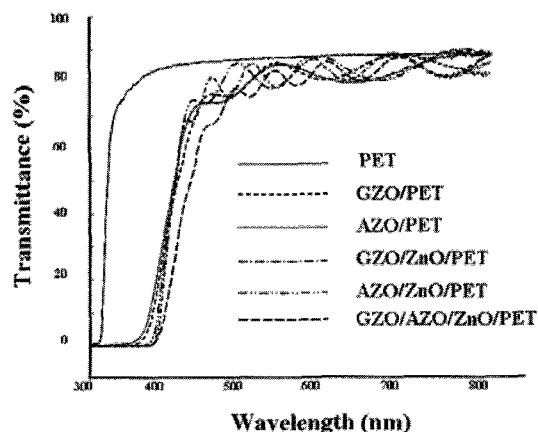
Transmittances of AZO, GZO, AZO/ZnO, GZO/ZnO, and GZO/AZO/ZnO films coated on PET substrates are presented in Fig. 7. Transmittances at the half-wave optical thicknesses of all specimens in the visible region are very close to that of substrate, indicating that the films are non-absorbing and transparent and the extinction coefficients of the films are on the order of 10^{-3} or less. Therefore, the optical constants of AZO, GZO, and ZnO films can be determined by an envelop method. Using the transmittance spectra and the envelop method, it is found that the refractive indices of AZO, GZO, and ZnO films are $n_{AZO} = 1.997$, $n_{GZO} = 1.953$, and $n_{ZnO} = 2.0$ at 550 nm, respectively. It seems that the small amounts of Al and Ga dopants in ZnO films do not induce a large change in the refractive index of the ZnO film, implying that the optical properties of AZO and GZO films are similar to that of ZnO films.

In the case of multilayer structures using ZnO films as buffer layers, such as AZO/ZnO/PET, GZO/ZnO/PET, and GZO/AZO/ZnO/PET, the transmittance spectra of the multilayer films show also interference fringes due to a small refractive index contrast among AZO, GZO, and ZnO films. Although appearance of the interference fringes is a multilayer effect, it seems that two- and three-

layers of AZO, GZO, and ZnO films on PET films can be treated as a single layer from a viewpoint of tranmittance. The effective indices of two- and three-layers are 1.987, 1.999, and 1.924 at 550 nm, respectively. The effective refractive index of GZO/AZO/ZnO/PET tends to decrease due to the interferences among the interfaces in the multilayer. For comparison, the average value of resistivity of the multilayer TCO films obtained in this work are more or less 80%, Whereas the average visible transmittance of ITO films deposited on polymer or glass is about 85%[10,13]. The visible part of the transmittance spectra of AZO and GZO deposited on polymer is reported to be in a range from 80 to 85%[15,16].

4. Conclusion

The transparent conducting oxide (TCO) films with a ZnO buffer layer showed better quality than those without a buffer layer in every sense. The crystal quality of the former is better than the latter, the electrical resistivity of the former is lower than the latter, and the transmittance property of the former is not inferior to the latter. The lowest resistivity(8.3×10^{-4} Ωcm) is obtained with a buffer layer thickness of 150nm for which the transmittance of GZO/AZO/ZnO/PET samples is higher than 85% regardless of the ZnO buffer layer thickness. On the other hand it was found that there was little difference in electrical, and optical properties between AZO, GZO and GZO/AZO films with a ZnO buffer layer.

References

[1] H. L. Hartnagel, A. L. Dawar, A. K.Jain, C. Jagadish, "Semiconduction Transparent Thin Films", Institute of Physics Publishing, Bristol and Philadelphia, (1995).

[2] M. Hiramatsu, K. Imaeda, N. Horio, and T Goto,"J. Vac. Sci. Technol. A"16, 669 (1998)

[3] M. Chen, Z. L. Pei, C. Sun, J. Gong, R.F. Huang, and L. S. Wen,"Mat. Sci. and Eng. B", 85, 212 (2001)

[4] T. Minami, H. Sato, H. Nanto, S. Takata,"Jpn. J. Appl. Phys."24, L781 (1985)

[5] Kaladex® 1020, "Dupont Teijin Films", Technical data sheet KXTD 005-K1020

[6] K. Ellmer, "J. Phys. D: Appl. Phys."33, R17-R32 (2000)

[7] M. Fahland, P. Karlsson, C. Charton, "Thin Solid Films."392, 334 (2001)

[8] X.W. Sun, L. D. Wang, H. S. Kwok, "Thin Solid Films."360, 75-81 (2000)

[9] M. Chen, Z.L. Pei, C. Sun, J. Gong, R.F. Huang, L.S. Wen," Mat. Sci&Eng. B"85, 212-217 (2001)

[10] C. Nunes de Carvalho, G. Lavareda, E. Fortunato, H. Alves, A. Goncalves, J. Varela, R. Nascimento, A. Amaral," Mat. Sci&Eng. B"118, 66-69 (2005)

[11] S. Yamamoto, T. Yamanaka, Z. Ueda,"J. Vac. Sci. Technol.", 5A, 1952 (1987)

[12] H. Nanto, T. Minami, S. Orito, S. Takaka,"J. Appl. Phys." 63, 2711 (1988)

[13] J C Manifacier, J Gasiot, and J P Fillard,"J. Phys."E9, 1002-1004 (1976)

[14] C. Guillen and J. Herrer. Appl. Phys,"101, 073514 (2007)

[15] E. Fortunato, P. Nunes, A. Marques, D. Costa, H. Aguas, I. Ferreira, M.E.V. Costa, M.H. Godinho, P.L. Almeida, J.P. Borges, R. Martins,"Surf. And Coat. Technol."151-152, 247-251 (2002)

[16] Elvira Fortunato, Alexandra Goncalves, Vitor Assuncao, Antonio Marques, Hugo Aguas, Luis Pereira, Isabel Ferreira, Rodrigo Martins,"Thin Solid Films"442, 121-126 (2003).