J Electroceram (2009) 23:554–558
DOI 10.1007/s10832-008-9539-6

Effects of substrate temperature on electrical and optical properties ITO films deposited by r.f. magnetron sputtering

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Received: 28 May 2007 / Accepted: 8 July 2008 / Published online: 28 July 2008

Abstract Indium tin oxide (ITO) films have been prepared by r.f. magnetron sputtering using powder target. X-ray diffraction analysis indicates that the deposited films were polycrystalline and retained a cubic bixbite structure. The ITO films deposited at low substrate temperature (T_s) exhibit a (411) preferred orientation but the films deposited at high T_s prefer a (111) orientation. The substrate temperature was found to significantly affect the electrical properties. As the T_s was increased, the conductivity of ITO films was improved due to thermally induced crystallization. The lowest resistivity (8.7×10^{-4} Ω-cm) was obtained from ITO films deposited at 450 °C. However, optical properties of the films were somewhat deteriorated. The infrared (IR) reflectance of the film increases with increasing the substrate temperature.

Keywords ITO film · Sputtering · Powder target · Substrate temperature

1 Introduction

Transparent conducting oxide (TCO) films have been attracting increasing interest since their great importance in a wide range of applications such as solar cell, liquid crystal displays and photodetectors, etc. [1–4]. Especially indium tin oxide (ITO) thin films have been widely used due to low resistivity, high transmittance, and good etching properties compared to other transparent conducting oxide films such as SnO_2 or ZnO [5–9]. ITO films have been fabricated by various methods; for example, spray pyrolysis, electron beam evaporation, chemical vapor deposition, magnetron sputtering, electron cyclotron resonance plasma sputtering. Among these techniques, magnetron sputtering is considered to be one of the best methods for preparing high-quality ITO films [10].

Meanwhile, ITO is more expensive than other TCO materials such as impurity doped ZnO and SnO2. Therefore, target utilization efficiency becomes increasingly critical when employing expensive target materials such as ITO [11]. The powder target has been used instead of the conventional ceramic target in order to improve the utilization efficiency of the target and reduce the cost of the film deposition processes [12–14]. However, the powder target causes a low electrical conductivity and brownish or black color which result in low transmittance in visible region. These properties of films cannot meet the demand of most of the optoelectronic devices. In order to obtain high-quality ITO films, it is necessary to prepared them at high temperature during deposition or post-deposition annealing treatment.

This work investigates the effects of the substrate temperature on the electro-optical properties of sputtered ITO films prepared by using powder target.

2 Experimental

ITO films were prepared by a commercial r.f. magnetron sputtering system. The chamber was pumped by a turbomolecular pump and the base pressure before deposition was about 1.3×10^{-3} Pa. ITO powders with SnO_2 content of 10°wt% were used as targets after slightly compressing them into a cupper holder, 3 in. in diameter. The substrate

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of Corning 7059 glass was placed on a substrate holder having heating block. The distance of target-substrate was 60°mm. The substrate was rotated with a constant speed above the target for film uniformity. Before the sputtering deposition, the pre-sputtering was carried out for 10°min under the same condition as the deposition. Sputtering deposition was carried out in a pure argon atmosphere at a r.f. power of 20 W and a pressure of 0.8°Pa. During the sputter deposition, the substrate was heated from room-temperature to 450 °C.

3 Results and discussion

ITO films prepared by using a powder target were physically stable and have good adherence to the substrate, regardless of substrate temperature.

XRD patterns of ITO films prepared at different substrate temperatures (T_s) are shown in Fig. 1. During the deposition, the other deposition conditions were kept constant. All the peaks can be assigned to the cubic bixbyite structure of In_2O_3. In these films, only In_2O_3 phase was detected from the X-ray pattern, which implies that tin replace indium substitutional in the lattice. The ITO film prepared at room temperature exhibits a weak peak at 2θ=38.1° corresponding to (4 1 1) plane of In_2O_3. The crystallization temperatures (T_c) of amorphous ITO films have been reported to be 160–180 °C [15, 16]. In the case of sputtering method, it was reported that some ITO films deposited at room temperature showed polycrystalline structure [17]. Whereas, in case of e-beam (EB) evaporation, amorphous ITO films could be obtained at T_s below the crystallization temperature [18, 19]. With increasing substrate temperature, the locations of the measured diffraction peaks do not change significantly, but they become more intense. In addition, new peak corresponds to (4 2 2) plane is shown at 2θ=44.3°. In the ASTM powder pattern for structure of In_2O_3, the relative intensities for the (4 1 1) and the (4 2 2) peaks are very low. In this study, at low substrate temperature (T_s<200 °C), the two peaks (4 1 1) and (4 2 2) appear prominently, indicating the coexistence of <4 1 1> and <4 2 2> textures. At the substrate temperature range between 200 and 300 °C, the (4 1 1) and (4 2 2) peak disappear and the (2 2 2) peak becomes very strong, resulting in a preferred orientation in the <1 1 1> direction. Kumar and Mansingh [20], in their work on r.f. sputtered ITO films, found that the structure and orientation of ITO films depended on the energy of the sputtered particles arriving at the substrate. They suggested that the thermalized sputtered atoms prefer to orientate in the (222) direction and the particles with higher energies prefer the (400) and (440) orientations depending on their energies. When the substrate is heated at 300 °C, the pattern of the ITO film exhibits three diffraction peaks corresponding to the reflections produced by the (2 2 2), (4 0 0), and (4 4 0) planes, respectively. The intensity of the (222) peak increases for films deposited at very high substrate temperature (T_s≥400 °C), which indicates that the crystallinity of the ITO film is improved and the grain sizes become larger with elevating substrate temperatures.

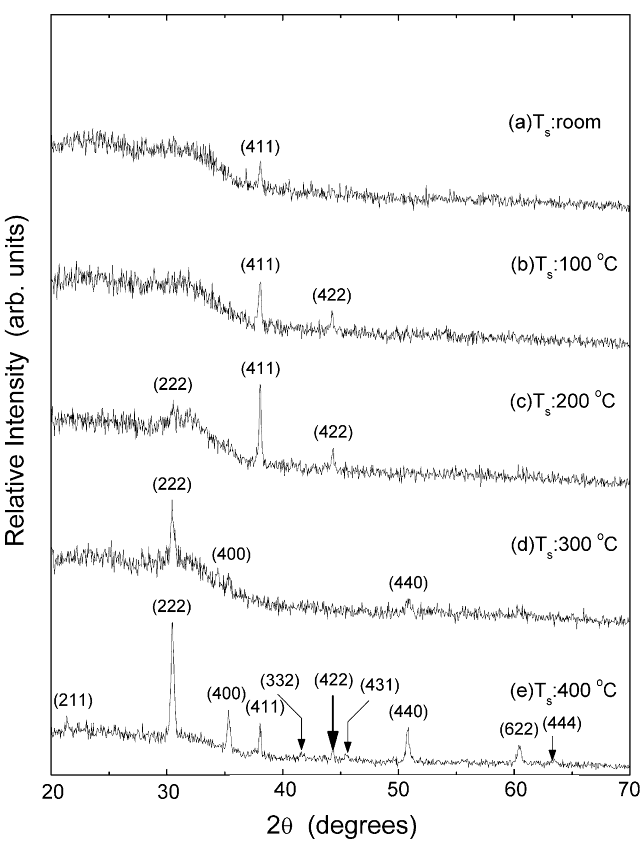

Fig. 1 XRD patterns for ITO films deposited at various substrate temperatures. The thickness of the films is about 100 nm

Table 1 presents XPS compositional analysis of ITO films deposited at various substrate temperatures. A lack of oxygen is observed in all samples and the film becomes more non-stoichiometric as the substrate temperature increases from room-temperature to 400 °C. It suggests

Table 1 XPS compositional analysis of ITO films as a function of substrate temperature.

Substrate temperature (°C)	Atomic concentration		
	X_{In}	X_{Sn}	X_O
Room temperature	38.3	4.6	57.1
100	39.8	5.2	55.0
200	34.7	4.5	60.8
300	40.0	5.8	54.2
400	41.5	5.2	53.3

that the number of oxygen vacancies increases at higher substrate temperature.

Figure 2 showed the relationship between the resistivity and the substrate temperature of ITO films. The resistivity of the films decreases with increasing the substrate temperature from room-temperature to 450 °C. The lowest resistivity (8.7×10^{-4} Ω-cm) was obtained from ITO films deposited at 450 °C. Although this value is higher than that ($1–6\times10^{-4}$ Ω-cm) of the film deposited using conventional ceramic target [21–25], the ITO films in this work is applicable to low cost transparent electrode for optoelectronic devices such as touch panel. The resistivity did not show significant temperature dependence, thus proving that the ITO films are degenerate semiconductors. The enhancement of the electrical properties of the films with increasing the substrate temperature was associated with the effect of thermally induced crystallization [26]. It was reported that amorphous ITO films were crystallized with annealing treatment over 150 °C [27]. In this study, the decrease of resistivity could be explained by the fact that ITO films showed better crystallinity with larger grain size and reduced the grain boundary scattering [28].

It is well known that the resistivity does not only depend on the electron concentration but also on the carrier Hall mobility. Figure 3 shows the carrier concentration (*N*) and the Hall mobility (μ) of the films as a function of substrate temperature. The direction of the Hall voltage shows that the electrons are the majority carriers in the ITO films. The carrier concentration monotonically increases from 1.15×10^{20} to 5.7×10^{20} °Cm^{-3}. For ITO films, the carrier concentration mainly originates from incomplete oxidation of the In–Sn alloy and substitution doping of tin. Meng et al. [29] suggested that the variation of the electron concentration does not result from the oxygen vacancies,

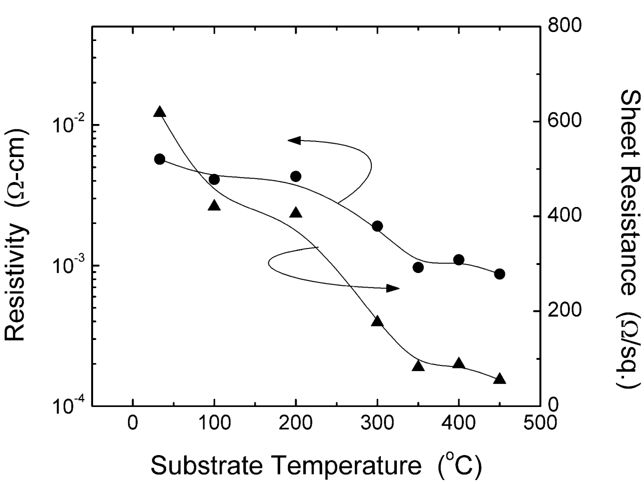

Fig. 2 Dependence of the substrate temperature on the resistivity of ITO films

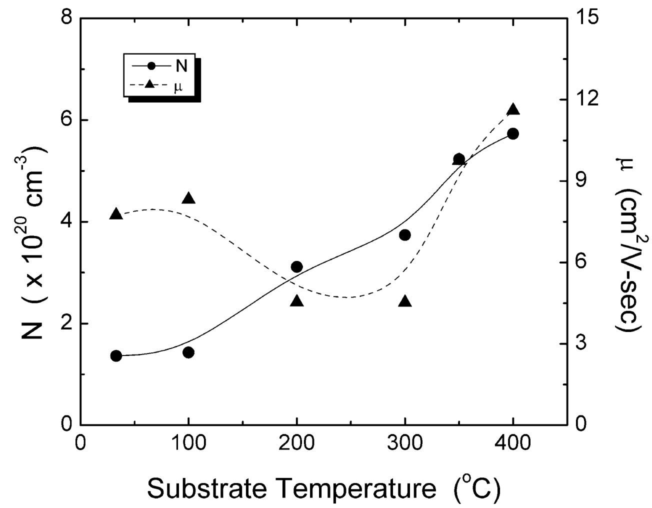

Fig. 3 Carrier concentration (*N*) and Hall mobility (μ) of ITO films as a function of substrate temperature

but from the tin atoms. The high substrate temperature may result in more tin atoms diffusing from grain boundaries and interstitial lattice locations to regular In_2O_3 lattice locations. As the tin atom has a higher valence than the indium atom has, they behave as donors in ITO films. Therefore, this kind of diffusion will give high electron concentration. Therefore, the increase in the carrier concentration is probably due to the increase in the number of oxygen vacancies and tin atoms, as seen in Table 1. In low substrate temperature range, the Hall mobility decreases with increasing substrate temperature and it reaches its minimum value at 300 °C. Further increase in the temperature causes an increase in the mobility. The Hall mobility in ITO films has a relation with XRD peak intensity, the films which have a high (2 2 2) peak intensity have a high Hall mobility [30]. From Fig. 1, it can be seen that the (2 2 2) peak appears at the 200 °C and is stronger with increasing substrate temperature. In addition, the grain growth at higher substrate temperature results in less grain boundary and, consequently, there is less grain-boundary scattering and thus the mobility of the charge carrier is enhanced.

The optical transmittance and the reflectance spectra in both visible and near-IR regions for ITO films prepared at various substrate temperatures is given in Fig. 4. For transmittance measurements the ITO films were irradiated under perpendicular angle of incidence. The reference used was air, i.e. the data presented in this work contain the transmittance of ITO including the glass substrate. The transmittance of the uncoated glass substrate is shown for comparison, also. The reflection measurements were carried out under an angle of incidence of 7°. Compared with the film prepared with conventional ceramic target, ITO films in this work exhibit a good transparency (80–90%) in

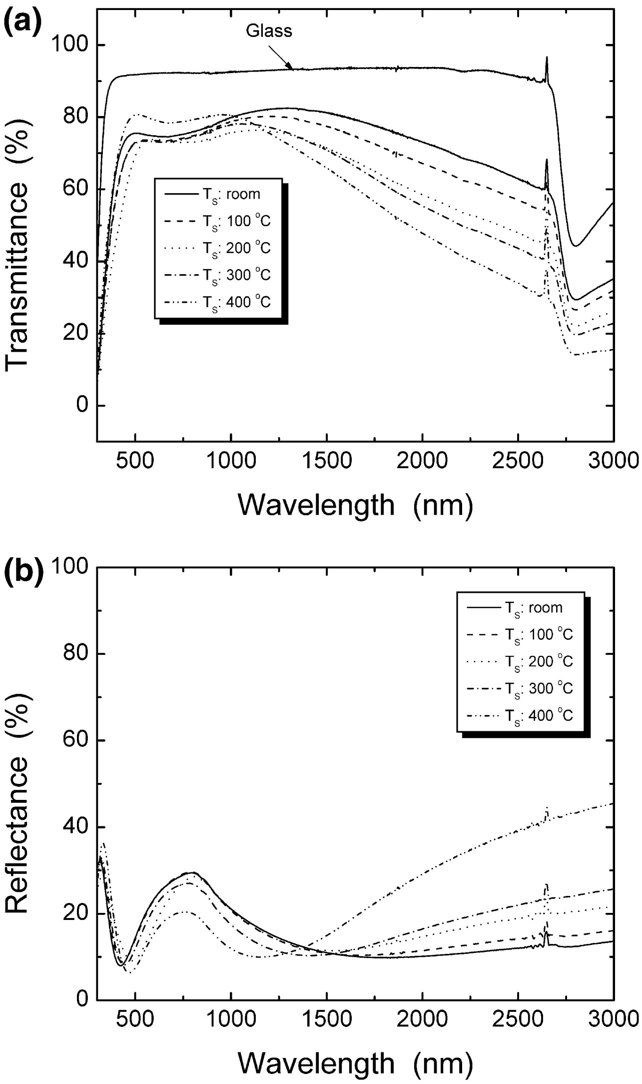

Fig. 4 Optical transmittance (**a**) and the reflectance (**b**) spectra of ITO films deposited at various substrate temperatures

visible regions when the transmittance spectrum of the ITO films is calculated by subtracting the transmittance of the uncoated glass substrate. The transmittance and the reflectance were found to decrease slightly in the visible region as the substrate temperature was increased. This reduction can be related to the structure of ITO films. As seen in Fig. 1, the (2 2 2) peak for ITO films deposited at higher substrate temperature was stronger and sharper, suggesting that the crystallinity of the films enhanced and the grain size increased. Therefore, the surface of ITO film becomes rough and results in more light scattered and then a low transmittance in the visible region. However, the transmittance enhances when the film is heated at 400 °C. At high substrate temperature, the structure of the films is improved and the defects decreases so that the transmittance of the film is increased. The spectrum also shows that the transmittance in the near infrared (IR) region decreases as the substrate temperature is increased. The dominant cause of transparency in this region is the reflection, as can be seen Fig. 4(b). In the near-IR region, the free carrier absorption becomes important for the transmittance and reflectance of the ITO films. The optical phenomena in this region can be explained on the basis of classical Drude theory. According to this theory, the transition from high transmittance to high reflectance is determined by the plasma oscillation of the free electrons and is shifted to shorter wavelengths as the free electron concentration is increased.

Figure 5 shows the infrared (IR) reflectance of the ITO films deposited at various substrate temperatures. The IR reflectance of the ITO films increases significantly as the substrate temperature is higher. Frank et al. [31] showed that the IR reflectance (R) can be expressed by

$$R = 1 - \frac{4\varepsilon_0 c_0}{e}\frac{1}{Nd\mu} \tag{1}$$

where c_0 is the velocity of light, ε_0 is the permittivity of free space, e is the electronic charge, N is the carrier concentration, d is the film thickness, and μ is the mobility of the free carriers. According to Eq. 1, the IR reflectance increases with the product of the carrier concentration N and carrier mobility μ. As seen in Figs. 2 and 3, the films grown at higher temperature have higher conductivity and larger values of the product $N\mu$ than those for lower substrate temperature. Therefore, the IR reflectance of the film increases with increasing the substrate temperature, as observed.

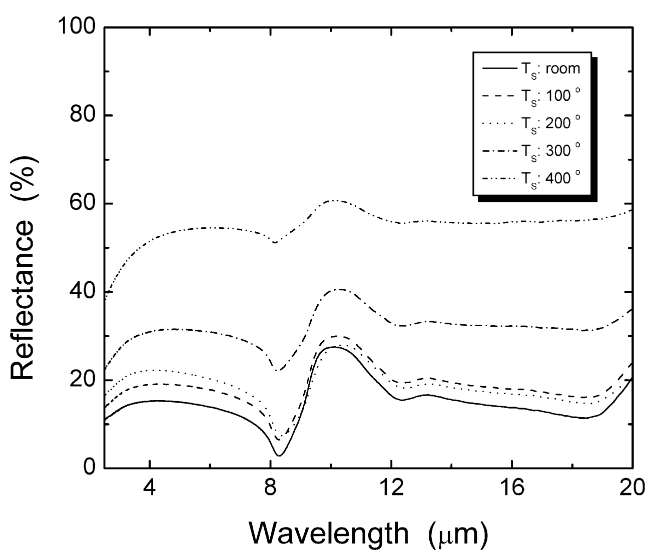

Fig. 5 IR reflectance of ITO films deposited at various substrate temperatures

4 Conclusion

ITO films have been deposited onto glass substrates by r.f. magnetron sputtering using power target. ITO films were polycrystalline and retained a cubic bixbite structure. The ITO films deposited at low substrate temperature exhibited the (411) preferred orientation but the films deposited at high temperature preferred the (111) orientation. As the substrate temperature was increased, (2 2 2) peak intensity was increased and the film tended to have a random orientation. The enhancement of the electrical properties of the films with increasing the substrate temperature was associated with the effect of thermally induced crystallization and the oxygen vacancies. The lowest resistivity (8.7×10^{-4} Ω-cm) was obtained from ITO films deposited at 450 °C. The transmittance and the reflectance were found to decrease slightly in the visible region as the substrate temperature was increased, which can be related to the structure of ITO films. The transmittance in the near infrared (IR) region was decreased as the substrate temperature was increased. The films grown at higher temperature had higher conductivity and larger values of the product of the carrier concentration and the mobility than those for lower substrate temperature. Therefore, the IR reflectance of the film was increased with increasing the substrate temperature. Although the electrical and optical properties of the ITO films prepared using powder target is somewhat worse than those deposited with a conventional ceramic target, the possibility of obtaining low-cost films shows prospective applications in optoelectronic and photovoltaic.

Acknowledgement This work has been supported by KESRI (R-2004-B-119), which is funded by MOCIE (Ministry of Commerce, Industry and Energy).

References

1. T.J. Coutts, X. Li, M.W. Wanlass, K.A. Emery, T.A. Cessert, IEEE Electron. Device Lett. **26**, 660 (1990)
2. M. Masuda, K. Sakuma, E. Satoh, Y. Yamasaki, H. Miyasaka, J. Takeuchi, in *Proc. 6th Int. Electronic Manufacturing Technology Symp.* (1989), p. 95
3. E. Takeda, T. Kawaguchi, Y. Nanno, H. Tsutsu, T. Tamura, S. Ishihara, et al., in *Proc. Int. Display Research Conf.* (1988), p. 155
4. P.P. Deimel, B.B. Heimhofer, G. Krotz, H.J. Lilienhof, J. Wind, G. Muller et al., IEEE Photon. Technol. Lett. **2**, 449 (1990). doi:10.1109/68.56637
5. Y.-S. Kim, Y.-C. Park, S.G. Ansari, J.-Y. Lee, B.-S. Lee, H.-S. Shin, Surf. Coat. Technol. **173**, 299 (2003). doi:10.1016/S0257-8972(03)00717-5
6. M.-S. Hwang, H.J. Lee, H.S. Jeong, Y.W. Seo, S.J. Kwon, Surf. Coat. Technol. **171**, 29 (2002). doi:10.1016/S0257-8972(03)00231-7
7. S.H. Keshmiri, M. Rezaee-Roknabadi, S. Ashok, Thin Solid Films **413**, 167 (2002). doi:10.1016/S0040-6090(02)00340-1
8. S. Ishibashi, Y. Higuchi, Y. Ota, K. Nakamura, J. Vac. Sci. Technol. A **8**, 1403 (1990). doi:10.1116/1.576890
9. I. Hamberg, C.G. Grangvist, J. Appl. Phys. **60**, R123 (1986). doi:10.1063/1.337534
10. W.-F. Wu, B.-S. Chiou, Thin Solid Films **298**, 221 (1997). doi:10.1016/S0040-6090(96)09311-X
11. H. Harada, Y. Kamatani, A. Hirata, T. Koyanagi, Jpn. J. Appl. Phys. **36**, 884 (1997). doi:10.1143/JJAP.36.884
12. Y. Zhou, P.J. Kelly, Thin Solid Films **469–470**, 18 (2004). doi:10.1016/j.tsf.2004.06.186
13. T. Minami, T. Yamamoto, Y. Toda, T. Miyata, Thin Solid Films **373**, 189 (2000). doi:10.1016/S0040-6090(00)01132-9
14. T. Minami, H. Sonohara, T. Kakumu, S. Takata, Thin Solid Films **270**, 37 (1995). doi:10.1016/0040-6090(95)06889-9
15. P.K. Song, H. Akao, M. Kamei, Y. Shigesato, I.Y. Asui, Jpn. J. Appl. Phys. **38**, 5224 (1999). doi:10.1143/JJAP.38.5224
16. C.W. Ow-Yang, D. Spinner, Y. Shigesato, D.C. Paine, J. Appl. Phys. **83**, 45 (1998)
17. R. Latz, B. Ocker, C. Daube, S.N. Daube, SID Dig. Technol. **24**, 975 (1993)
18. Y. Shigesato, S. Takaki, T. Haranoh, J. Appl. Phys. **71**, 3356 (1992). doi:10.1063/1.350931
19. T. Oyama, N. Hashimoto, J. Shimizu, Y. Akao, H. Kojima, K. Aikawa et al., J. Vac. Sci. Technol. A **10**, 1682 (1992). doi:10.1116/1.577769
20. C.V.R. Vansant Kumar, A. Mansingh, J. Appl. Phys. **65**, 1270 (1989). doi:10.1063/1.343022
21. S. Calnan, H.M. Upadhyaya, M.J. Thwaites, A.N. Tiwari, Thin Solid Films **515**, 6045 (2007). doi:10.1016/j.tsf.2006.12.063
22. M. Stowell, J. Müller, M. Ruske, M. Lutz, T. Linz, Thin Solid Films **515**, 7654 (2007). doi:10.1016/j.tsf.2006.11.166
23. C.-H. Yang, S.-C. Lee, S.-C. Chen, T.-C. Lin, Mater. Sci. Eng. B **129**, 154 (2006). doi:10.1016/j.mseb.2006.01.012
24. T.-C. Lin, C.-C. Chang, C.-F. Chiu, Mater. Sci. Eng. B **129**, 39 (2006). doi:10.1016/j.mseb.2005.12.013
25. C. Guillén, J. Herrero, Vacuum **80**, 615 (2006). doi:10.1016/j.vacuum.2005.10.006
26. C.H. Yi, Y. Shigesato, I. Yasui, S. Takaki, Jpn. J. Appl. Phys. **34**, L244 (1995). doi:10.1143/JJAP.34.L244
27. D.C. Paine, T. Whitson, D. Janiac, R. Beresford, C.O. Yang, B. Lewis, J. Appl. Phys. **85**, 8445 (1999). doi:10.1063/1.370695
28. H. Kim, J.S. Horwitz, G. Kushto, A. Pique, Z.H. Kafafi, C.M. Gilmore et al., J. Appl. Phys. **88**, 6021 (2000). doi:10.1063/1.1318368
29. L.J. Meng, M.P. dos Santos, Thin Solid Films **322**, 56 (1998). doi:10.1016/S0040-6090(97)00939-5
30. L.J. Meng, M.P. dos Santos, Thin Solid Films **289**, 65 (1996). doi:10.1016/S0040-6090(96)08892-X
31. G. Frank, E. Kauer, H. Köstlin, Thin Solid Films **77**, 107 (1981). doi:10.1016/0040-6090(81)90365-5