
ELSEVIER
Journal of
ALLOYS
AND COMPOUNDS
An Interdisciplinary Journal
of Materials Science and
Solid-State Chemistry and Physics

Journal of Alloys and Compounds 550 (2013) 258–262

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Influence of the substrate bias voltage on the physical properties of dc reactive sputtered Ta_2O_5 films

K. Cang [a,b], L.Y. Liang [b], Z.M. Liu [b], L. Wu [b], H. Luo [b], H.T. Cao [b,*], Y.S. Zou [a,*]

[a] *School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China*
[b] *Division of Functional Materials and Nano Devices, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China*

ARTICLE INFO

Article history:
Received 25 July 2012
Received in revised form 24 September 2012
Accepted 26 September 2012
Available online 5 October 2012

Keywords:
Ta_2O_5 dielectric films
Magnetron sputtering
Spectroscopic ellipsometer
Dielectric loss

ABSTRACT

Tantalum oxide (Ta_2O_5) films were deposited on ITO glass substrates by dc reactive magnetron sputtering in oxygen/argon gas mixture. The performance of Ta_2O_5 films deposited at different substrate bias voltages in the range from 0 to -145 V was investigated in detail. Our results show a decrease both in the film porosity and the surface roughness as the substrate bias voltage changes within a certain scope, which interestingly leads to a conspicuous improvement of their electrical properties. Further increasing of the negative bias voltage, however, results in deterioration of the film packing density, surface morphology, and leakage current as well. Under the optimal substrate biasing condition (-135 V), the Ta_2O_5 films exhibit attractive electrical properties, namely a permittivity value as high as $\sim$23, a dielectric loss of $\sim$0.01, and a leakage current density as low as 1.45×10^{-7} A/cm^2 at 1 MV/cm.

1. Introduction

Present semiconductor technology demands continuous shrinkage of the device dimensions and improvement of its performance [1–3]. Amorphous oxide thin-film transistors (TFTs) have attracted ever-increasing attention as backbone electronics for active-matrix liquid crystal displays (AMLCDs) and active-matrix organic light-emitting diode displays (AMOLEDs). Basically, oxide TFTs provide two principal advantages over traditional Si-based TFTs: less energy consumption during fabrication and lower cost [4–7]. As a key element in TFTs, qualified high permittivity (high k) dielectrics determine the performance of the device [8]. In the search for a replacement of silicon dioxide films, various high k dielectric materials such as titanium oxide (TiO_2), zirconium oxide (ZrO_2), hafnium oxide (HfO_2) and tantalum oxide (Ta_2O_5) [9–11] were investigated for microelectronic applications. Among them, Ta_2O_5 has been considered as a promising candidate due to its high permittivity, large refractive index, excellent step coverage and tolerable dielectric strength [12–15], and then has stimulated intensive research activities [16,17].

Various deposition techniques such as thermal evaporation, reactive magnetron sputtering, ion-assisted electron beam evaporation, chemical vapor deposition, pulsed laser deposition, atomic layer deposition, ion beam deposition and metal-organic chemical vapor deposition [18–24] were employed for the fabrication of Ta_2O_5 films. Among them, reactive magnetron sputtering has the advantage of the preparation of large area uniform films with relatively high growth rate [25]. Especially, the substrate biasing-assisted sputtering process can offer a new degree of freedom to tune the film properties more subtly. As a result, a few studies explored the effect of substrate bias on the properties of sputtered Ta_2O_5 films on Si substrates, and a monotonically improvement of the electrical properties with increasing substrate bias voltage was observed [26,27]. However, the growth and physical properties of oxide films on ITO glass are different from those on silicon wafer, since the ITO glass has a quite rougher surface compared to Si. In this investigation, an attempt is carried out to prepare Ta_2O_5 films by dc reactive magnetron sputtering technique on ITO glasses under various substrate bias voltages without intentional substrate heating. The influence of substrate bias voltage on the structural, optical, and dielectric properties was studied systematically. It is found that, a proper substrate bias voltage can densify the bulk film, smoothen the film surface, and improve the dielectric properties, which offers an opportunity to realize high k dielectrics on ITO glass for transparent electronics application.

2. Experimental

Prior to the deposition of Ta_2O_5 films, the ITO glass substrates were ultrasonically cleaned with acetone (10 min), alcohol (10 min), and deionized water (10 min) sequentially for three times. The Ta_2O_5 films were deposited by dc reactive magnetron sputtering using a commercially available tantalum metallic target (2 in. diameter, 5 mm thickness, 4 N purity) under a base pressure of $\sim 10^{-5}$ Pa. The distance between the substrate and the target is 14.5 cm and the substrate is unintentionally

---

* Corresponding authors.
E-mail addresses: h_cao@nimte.ac.cn (H.T. Cao), yshzou75@gmail.com (Y.S. Zou).

0925-8388/$ - see front matter Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2012.09.134

heated during deposition. Before sputtering, the Ta target was pre-sputtered for about 20 min to get rid of the contamination on the target surface. The sputtering power was kept at 80 W, and the Ar/O_2 gas flow ratio was fixed to 7:3 while the total sputtering pressure was adjusted to be 0.45 Pa. The Ta_2O_5 films were deposited under various substrate bias voltages (V_S) ranging from 0 to −145 V by keeping the other process parameters as constant. Then metal/insulator/metal (MIM) capacitors were fabricated on the Ta_2O_5/ITO samples for the test of leakage currents and dielectric properties. Ti/Au (100/20 nm) top electrodes were deposited by electron beam evaporation through a shadow mask with a contact area of 3.14×10^{-4} cm^2.

The thickness and optical properties were analyzed by a spectroscopic ellipsometer (SE, J.A.Woollam Inc., M-2000DI) with a spectrum response ranging from 190 nm to 1700 nm at incidence angles of 55°, 65° and 75°. A film thickness of ~120 ± 5 nm was obtained with the same deposition time, implying that the substrate bias voltage has a marginal effect on the thickness. The surface morphology was examined via an atomic force microscopy (AFM, Veeco Dimention 3100). The leakage currents were measured with a semiconductor parameter analyzer (Keithley 4200-scs) in the dark at room temperature. The dielectric characteristics were measured with frequency in the range of 1 kHz–2 MHz using an impedance analyzer (Solartron SI 1260).

3. Results and discussion

3.1. Optical properties

The optical properties of Ta_2O_5 films, such as refractive index (n), absorption coefficient and band gap, were simulated by SE. The quality of the fitted results was assessed by the mean-squared-error (MSE) function, of which the values are always smaller than 10 so as to assure the reliability.

The dependence of the refractive index of Ta_2O_5 films on the substrate bias voltages is demonstrated in Fig. 1. For clarity, the refractive index at 2.25 eV is also plotted as an inset in Fig. 1. It shows that, the n value rapidly increases and tends to be saturated (~2.12) and then decreases when $|V_S| > 135$ V. Refractive index is closely related to the film density, which can be expressed by introducing the Drude equation [28]:

$$1 - p = \frac{n_f^2 - 1}{n_b^2 - 1} \qquad (1)$$

where n_f is the refractive index of porous materials (here, using the n value at 2.25 eV of the fabricated Ta_2O_5 films), n_b the refractive index of bulk material (n_b at 2.25 eV of bulk Ta_2O_5 is ~2.16 [29]), and p the mean value of the porosity, respectively. Based on Eq. (1), the porosity p of the films under various V_S was calculated and displayed in the inset of Fig. 1. A relative small p value of ~4.7% was obtained for the film at $V_S = -135$ V. The optical band gaps, another important factor for high k dielectrics, were calculated to be ~4.3 eV (in-between the reported values of 4.2–4.4 eV [30]), indicating a negligible change of the band gap for the Ta_2O_5 films in this study.

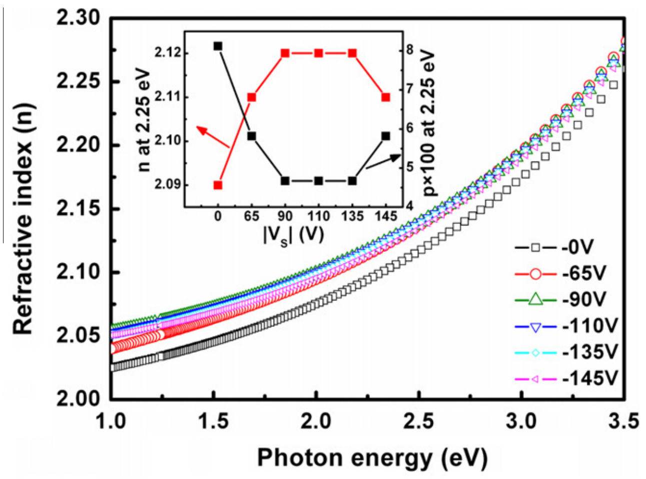

Fig. 1. The dependence of refractive index (n) of Ta_2O_5 films on the substrate bias voltage as a function of photon energy. The inset shows the n and p values as a function of substrate bias voltage.

3.2. Surface morphology

AFM images with scan areas of 1 μm^2 and 5 μm^2 were collected to examine the surface morphologies of the Ta_2O_5 films. Fig. 2 shows the typical surface morphologies of the films grown under substrate bias voltages of 0 V, −90 V, −135 V and −145 V, respectively. Obviously, the film grown under −135 V has a much more regular and uniform surface, while a roughened surface composed of peaks separated by valleys is observed on the other films. This appearance is also reflected by the variation of the root-mean-square (RMS) roughness, as demonstrated in Fig. 3. It is evident that the film grown under −135 V exhibits a smaller RMS roughness compared to the other films. This significant change of RMS roughness can be attributed to the favorable atom diffusion and migration on the growing surface.

3.3. Electrical properties

3.3.1. Leakage current

Fig. 4 represents the leakage current density–applied electric field (J–E) characteristics of (Ti/Au)/Ta_2O_5/ITO MIM capacitors. It is defined that top (bottom) injection mode is the direction of current flowing from top (bottom) electrodes into bottom (top) electrodes. The asymmetry of leakage current curves between the top and bottom injection modes is ascribed to the difference of the two Ta_2O_5/electrode interfaces. It is obvious that the films prepared by bias-assisted sputtering have much lower leakage current than the film without substrate bias. As shown in the inset of Fig. 4, leakage current density gradually decreases to the minimum at $V_S = -135$ V and then rebounds with further increasing of V_S. The lowest leakage current (top injection mode) density of 1.45×10^{-7} A/cm^2 was obtained at an electric field of 1 MV/cm under a substrate bias voltage of −135 V, indicating that a much lower defect concentration is present in that film.

3.3.2. Dielectric characteristics

The dielectric constant (ε_r) and dielectric loss ($\tan\delta$) are very important physical parameters for dielectric materials [31]. The dielectric constant of the films was calculated from the capacitance–voltage measurement using the following relation [32],

$$\varepsilon_r = C \cdot d / \varepsilon_0 \cdot A \qquad (2)$$

where C is the capacitance, d the thickness of the dielectric, A the area of the electrode, and ε_0 the permittivity of the free space, respectively. Fig. 5 shows the dependence of the dielectric constant of the Ta_2O_5 films grown at different substrate bias voltages on the frequency. It shows that the dielectric constant of the unbiased film is totally bigger than those of the bias-assisted sputtered films in the measured range. In the frequency range less than 10^6 Hz, the dielectric constant mainly depends on the space charge polarization which is related to electric polarization arising from the mobile and trapped charges in the amorphous or polycrystalline solids or in materials with a lot of traps involved [33,34]. Consequently, the lower dielectric constants in the bias-assisted sputtered films might be ascribed to the reduced trap states which also give rise to the decrease of the leakage current density mentioned above. The dielectric constant of the unbiased film rapidly decreases with increasing frequency (severe frequency dispersion of the dielectric constant), whereas the films prepared by bias-assisted sputtering have much weaker frequency dispersion of the dielectric constant, which is not only due to the repair of oxygen vacancies and bond defects in the initial oxide but also the improvement of the interface properties [35]. The dielectric constant of the Ta_2O_5 films whether

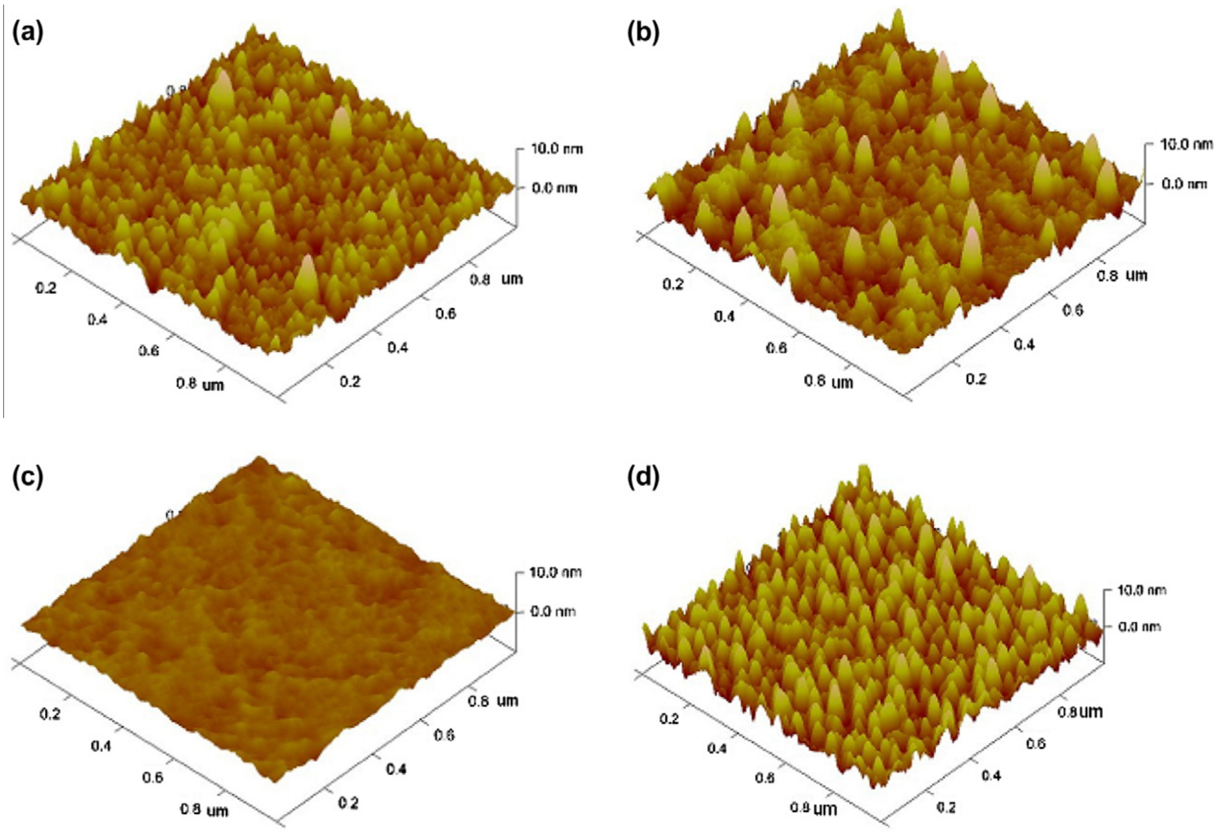

Fig. 2. Representative AFM images of the Ta_2O_5 films grown under a substrate bias voltage of (a) 0 V, (b) −90 V, (c) −135 V and (d) −145 V with a scan area of 1 μm^2.

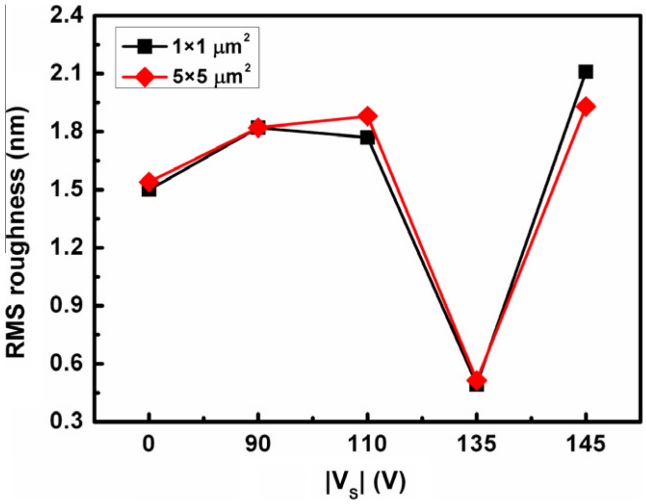

Fig. 3. The RMS roughness of all the Ta_2O_5 films as a function of substrate bias voltage.

at 10 kHz or at 1 MHz firstly displays a downward trend and then fluctuates around ∼25 with varying the substrate bias voltages, as shown in the inset of Fig. 5. The measured dielectric constants are similar to the values of 22–28 [36–40] reported in the literature except for the unbiased film.

Dielectric loss represents the lost energy that is converted into heating eventually in a dielectric material when placed in an alternating current electrical field. The plot of dielectric loss ($\tan\delta$) *vs.* frequency is exhibited in Fig. 6. The dielectric loss of the films deposited under 0 V and −65 V gradually decreases with increasing

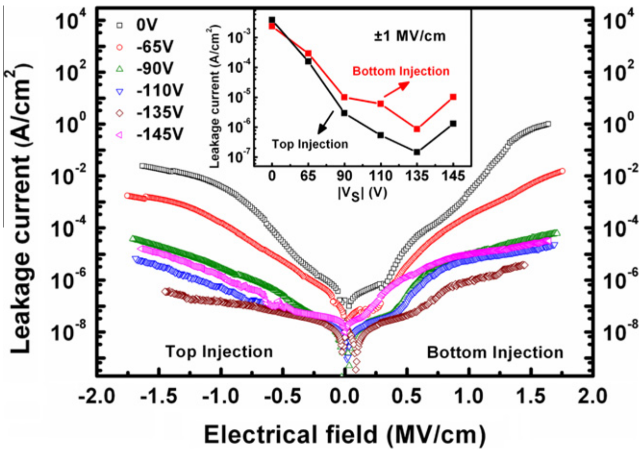

Fig. 4. Comparison of *J–E* characteristics of all the samples. The inset shows the leakage current density at ±1 MV/cm.

frequency in the lower frequency range (<∼10^5 Hz) and then increases at higher frequencies, which is thought to be caused by the presence of higher leakage currents [41]. The dielectric loss of the other films changes little in the lower frequency range (<∼10^5 Hz), but increases at the frequencies higher than 1 MHz. It is clear that in the whole measured range, the bigger the substrate bias voltage used, the smaller the dielectric loss obtained. When $|V_S|$ exceeds 90 V, the plots are almost merging together, and the dielectric loss approaches a relatively small value (∼0.01 at 1 kHz). This behavior is thought to be associated with the presence of considerably small leakage currents in these films [41], as manifested in Fig. 4.

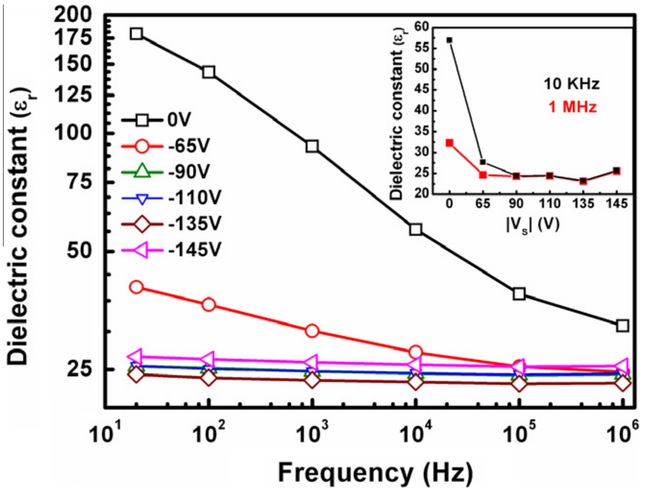

Fig. 5. Dielectric constant of the films as a function of frequency. The inset shows dielectric constants at 10 kHz and 1 MHz.

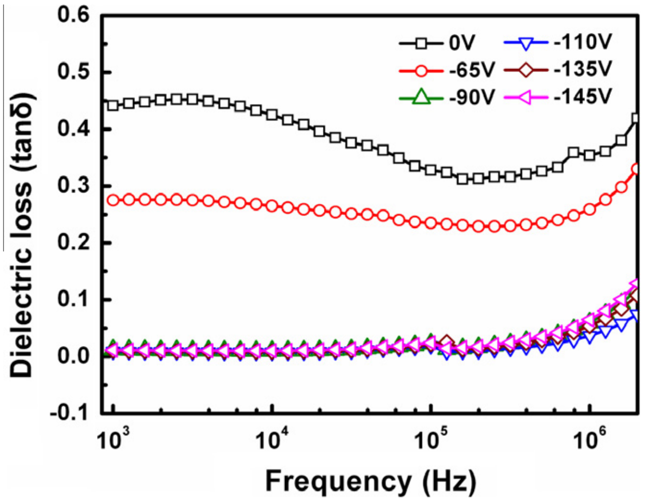

Fig. 6. The variation of dielectric loss with the frequency at different substrate bias voltages.

4. Discussion

The electrical properties of Ta_2O_5 films are closely coupled with the film density, crystallinity, and surface morphology [42]. The structural characterizations of the Ta_2O_5 films provide deep insights to understand the effect of the substrate bias voltage on their electrical properties. It is proved that Ta_2O_5 films deposited at $V_S = -135$ V have enhanced packing density with flat surface morphology. Generally, proper ion bombardment conditions (through substrate bias) favor the growth of more densely packed films and reduce the presence of pores and microvoids, thereby restraining the absorption of moisture, other gaseous contaminants, and the generation of defect state eventually. The evolution of the film density and surface morphology is believed to be a result of the beneficial 'soft-hammering' effect of ion bombardment, which can contribute to activate the mobility of the adatoms arriving onto the growing film surface. That is to say, the deposited atoms under a suitable substrate bias have high kinetic energy enough to diffuse more freely on the film surface and to occupy or approach the equilibrium lattice position. But nevertheless, a further increase of the substrate bias voltage ($|V_S| > 135$ V) is found to be accompanied with a deterioration of both the structural and the electrical properties. It is believed that the excessive energetic Ar ion bombardment, being analogous to overshoot, causes either some Ar ions incorporation into the growing films or the creation of some oxygen vacancies in the films (as a result of preferential oxygen sputtering which is well known to occur for oxides [43,44]). The presence of such Ar impurities and, more importantly, O vacancies is a highly plausible explanation for the noticeable electrical degradation for the films deposited with higher substrate bias voltages (see Fig. 4). These results highlight the crucial role of substrate bias voltage to optimize the microstructure, and hence, the electrical properties of the Ta_2O_5 films.

5. Conclusions

In summary, we have investigated the influence of substrate bias voltage on the optical, structural and electrical performance of Ta_2O_5 thin films deposited on ITO glass substrates. It is found that the relatively proper ion bombardment caused by a moderate substrate bias voltage densifies and smoothens the films and then improves their electrical properties. Under an optimal substrate biasing condition ($V_S = -135$ V), Ta_2O_5 films exhibit attractive physical properties, i.e., relatively large refractive index (~2.12) and a flat surface (RMS roughness ~0.5 nm), a permittivity of 23, a small dielectric loss (~0.01) and a low leakage current density of 1.45×10^{-7} A/cm^2 at 1 MV/cm. Thus, it can be concluded that the use of a suitable substrate bias voltage is an effective method to fabricate high-quality Ta_2O_5 gate dielectrics on ITO glass for transparent electronics applications.

Acknowledgements

This work is supported by the Chinese National Program on Key Basic Research Project (2012CB933003), the National Natural Science Foundation of China (Grant No. 11104289), the Science and Technology Innovative Research Team of Ningbo Municipality (2009B21005), the Key Program for Science and Technology Innovative Team of Zhejiang Province (2010R50020), and Applied Research Funds for Public Welfare Project of Zhejiang Province (2011C21030).

References

[1] S.Y. Tsai, Y.M. Lu, M.H. Hon, J. Phys. Conf. Ser. 100 (2008) 042030.
[2] R. Chau, J. Brask, S. Datta, G. Dewey, M. Doczy, B. Doyle, J. Kavalieros, B. Jin, M. Metz, A. Majumdar, M. Radosavljevic, Microelectron. Eng. 80 (2005) 1.
[3] E.P. Gusev, E. Cartier, D.A. Buchanan, M. Gribelyuk, M. Copel, H. Okorn-Schmidt, C.D'. Emic, Microelectron. Eng. 59 (2001) 341.
[4] R. Navamathavan, C.K. Choi, S.J. Park, J. Alloys Compd. 475 (2009) 889.
[5] H.Z. Zhang, L.Y. Liang, A.H. Chen, Z.M. Liu, Appl. Phys. Lett. 97 (2010) 12.
[6] J.F. Wager, Science 300 (2003) 1245.
[7] W.H. Ha, M.H. Choo, S. Im, J. Non-Cryst. Solids 303 (2002) 78.
[8] Z. Yu, L.Y. Liang, Z.M. Liu, W.Y. Xu, X.L. Sun, H.T. Cao, J. Alloys Compd. 509 (2011) 5810–5815.
[9] J. Robertson, Rep. Prog. Phys. 69 (2006) 327.
[10] Chen Yang, Huiqing Fan, Yingxue Xi, Jin Chen, Zhuo Li, Appl. Surf. Sci. 254 (2008) 2685–2689.
[11] Yingxue Xi, Huiqing Fan, Weiguo Liu, J. Alloys Compd. 496 (2010) 695–698.
[12] I. Kim, S. Ahn, B. Cho, J.Y. Lee, J.S. Chun, W. Lee, Jpn. J. Appl. Phys. Part 1 (33) (1994) 6691.
[13] E. Atanassova, N. Novkovski, A. Paskaleva, Solid-State Electron. 46 (2002) 1887.
[14] Y.M. Li, J.W. Lee, Comput. Phys. Commun. 147 (2002) 21.
[15] G.B. Alers, R.M. Fleming, A. Pinczuk, Appl. Phys. Lett. 72 (1998) 1308.
[16] T. Kato, T. Ito, J. Electrochem. Soc. 135 (1988) 2586.
[17] H. Zhang, R. Solanki, J. Appl. Phys. 87 (2000) 1921.
[18] A. Pignolet, G. Mohan Rao, S.B. Krupanidhi, Thin Solid Films 258 (1995) 195.
[19] E. Atanassova, G. Aygun, R. Turan, Tz. Babeva, J. Vac. Sci. Technol. A 24 (2006) 206.
[20] A.P. Huang, S.L. Xu, M.K. Zhu, B. Wang, H. Yan, T. Liu, Appl. Phys. Lett. 83 (2003) 3278.
[21] N. Gillard, L. Pinzelli, M.G. Jean, Appl. Phys. Lett. 89 (2006) 137506.
[22] N. Novkovski, E. Atanassova, A. Paskaleva, Appl. Surf. Sci. 253 (2007) 4396.
[23] F. Piret, M. Singh, C.G. Takoudis, B.L. Su, Chem. Phys. Lett. 453 (2008) 87.

[24] K. Tajima, Y. Yamada, S. Bao, M. Okada, K. Yoshimura, Sol. Energy Mat. Sol. Cells 92 (2008) 120.
[25] A.X. Wei, Z.X. Ge, X.H. Zhao, J. Liu, Y. Zhao, J. Alloys Compd. 509 (2011) 9758–9763.
[26] S.V. Jagadeesh Chandra, M. Chandrasekhar, G. Mohan Rao, S. Uthanna, J. Mater. Sci.: Mater. Electron. 20 (2009) 295–300.
[27] A.P. Huang, Paul K. Chu, J. Appl. Phys. 97 (2005) 114106.
[28] B.E. Yoldas, Appl. Opt. 19 (1980) 1425.
[29] H. Szymanowski, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu, J. Vac. Sci. Technol. A 23 (2005) 241–247.
[30] C. Chaneliere, J.L. Autran, R.A.B. Devine, B. Balland, Mater. Sci. Eng. R22 (1998) 269–322.
[31] X.S. Fang, C.H. Ye, L.D. Zhang, T. Xie, Adv. Mater. 17 (2005) 1661–1665.
[32] S.M. Sze, Physics of Semiconductor Devices, Wiley, New York, 2004.
[33] A. Elshafie, H.H. Afify, A. Abdel-All, Phys. Stat. Sol. 174 (1999) 301.
[34] Kwan Chi Kao, Dielectric Phenomena in Solids, Elsevier Academic Press, 2004.
[35] A. Paskaleva, E. Atanassova, N. Novkovski, M.P. Gjorgjevich, Proceeding of the 23rd International Conference on Microelectronics, vol. 2, MIEL, 2002.
[36] S.M. Gubanski, D.M. Huges, Thin Solid Films 52 (1978) 119.
[37] E. Kaplan, M. Balog, D.F. Bentchkowsky, This Journal 123 (1976) 1570.
[38] D.J. Smith, L. Young, IEEE Trans. Electron Dev. ED-28 (1981) 22.
[39] P.L. Young, J. Appl. Phys. 47 (1976) 242.
[40] P.L. Young, J. Appl. Phys. 47 (1976) 235.
[41] D. Brassard, M.A. El Khakani, J. Appl. Phys. 102 (2007) 034106.
[42] Y.B. Chen, C.L. Huang, Surf. Coat. Technol. 201 (2006) 654.
[43] N. Jiang, H.J. Zhang, S.N. Bao, Y.G. Shen, Z.F. Zhou, Physica B (Amsterdam) 352 (2004) 118.
[44] M.M. Yang, T.M. Reith, C.J. Lin, J. Vac. Sci. Technol. A 8 (1990) 3925.