Thickness dependence of refractive index for anodic aluminium oxide films

RE-LONG CHIU*, PENG-HENG CHANG
Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan

Anodic oxide films on aluminium have been employed in a variety of devices such as solar cell [1], sensors [2] and thin film transistor liquid crystal display (TFT/LCD) [3]. It was reported [3, 4] that anodic aluminium oxide film is a solution to depress hillock formation. Thin film transistors with Al gates and anodic $Al_2O_3 + Si_3N_4$ double layer gate insulators have been successfully fabricated in an 10.4-inch diagonal multicolour LCD display panel [3]. Consequently, much progress has been made in understanding the structure [5, 6], composition [7–10] and electrical properties [6, 7] of anodic aluminium oxide. In previous work it has been shown that an anodic oxide layer formed on pure Al without any prior heat treatment exhibits better dielectric properties, uniformity, and stability than oxide layers formed on Al pre-annealed at 410 °C [6]. Si or Cu doping of Al film was also found to reduce the quality of the anodic oxide layer [5]. For device application, the control of anodic film thickness and uniformity is very important. There are many methods to evaluate the thickness of an anodic oxide film, such as coulometry [11], transmission electron microscopy (TEM), ellipsometry [12], impedance [11], spectrophotometry [13], photoluminescence [14] etc. Coulometry is most convenient for anodic oxide film thickness determination, the thickness being calculated from the charge consumption based on Faraday's law. The calculated thickness, however, is subjected to uncertainties due to non-ideal current efficiency, roughness of the electrode, film non-stoichiometry, and error in the presumed film density. TEM offers a direct and absolute measurement of film thickness, but is time consuming and destructive. Ellipsometry can determine not only the thickness but also the refractive index of the film [12, 15]. For a top surface layer on a substrate with given optical properties the evaluation of both thickness and refractive index requires the numerical solution of two complex simultaneous equations, and the accuracy of the thickness results depends sensitively on the calculated refractive index [12]. If, however, either the thickness or the refractive index of the top film is known precisely then the numerical solution of the other quantity can be greatly simplified and its accuracy significantly increased. The purpose of this study is to measure the thickness of anodic Al_2O_3 films precisely by cross-sectional TEM techniques and then use the thickness value to fit the ellipsometry data for the unique solution of refractive index as a function of film thickness. This calculation is made possible by the assumption that the extinction index of the Al_2O_3 film is zero, or in other words, the film is non-absorbing. Dell'oca [16] has carefully studied anodic Al_2O_3 films formed on evaporated Al films ellipsometrically and showed that the non-absorbing model fits his experimental data the best. He estimated the extinction index of anodic Al_2O_3 film to be 0.002. The error in the calculated refractive index is about 0.01 if the extinction index is 0.002 instead of zero. The effect of absorption may be neglected since it affects the refractive index by less than 0.6%. We hope that the refractive index data obtained in the present study can be used in device applications for quick and precise thickness measurement by ellipsometry.

Sample preparation is similar to that described previously [5–6]. A 300 nm thick pure Al film was sputtered by DC magnetron on BPSG(borophosphosilicate glass)/SiO_2/Si substrates. The substrates were 4-inch diameter, p-type, 〈1 0 0〉 Si wafers. Wafers were anodized after the metal deposition without any heat treatment, and the anodization was conducted at room temperature in an AGW electrolyte [6] (AGW electrolyte is a mixture of 3% aqueous solution of taitaric acid and propylene glycol at a volume ratio of 2:8). The wafers were anodized, one at at time, at constant current mode (current density = 0.4 mA/cm^2) initially until reaching 100 V, then the anodizing was automatically switched to constant voltage mode until a preset time was reached. To monitor the anodic oxide growth, specimens were anodized for different durations varying from 3.5 to 30 min. TEM samples were prepared for film thickness measurement by ion milling in the usual fashion [17] and examined with a Philips CM20 microscope operating at 200 kV. Using the thickness data obtained from the TEM analysis the refractive index of the anodic oxide film was evaluated by ellipsometry. A Rudolph Research Auto EL-ILL ellipsometer using an He–Ne laser at a wavelength of 632.8 nm was employed for ellipsometry with an incident angle of 70°. The refractive index (n) and extinction coefficient (k) for the substrate aluminium are presumed to be 1.3 and 6.5, respectively [16].

Fig. 1a, b, c and d show the morphology of Al_2O_3

*Present address: Industrial Technology Research Institute, Electronics Research and Service Organization, 195 Section 4 Chung Hsing Road, Chutung, Hsinchu 31015, Taiwan.
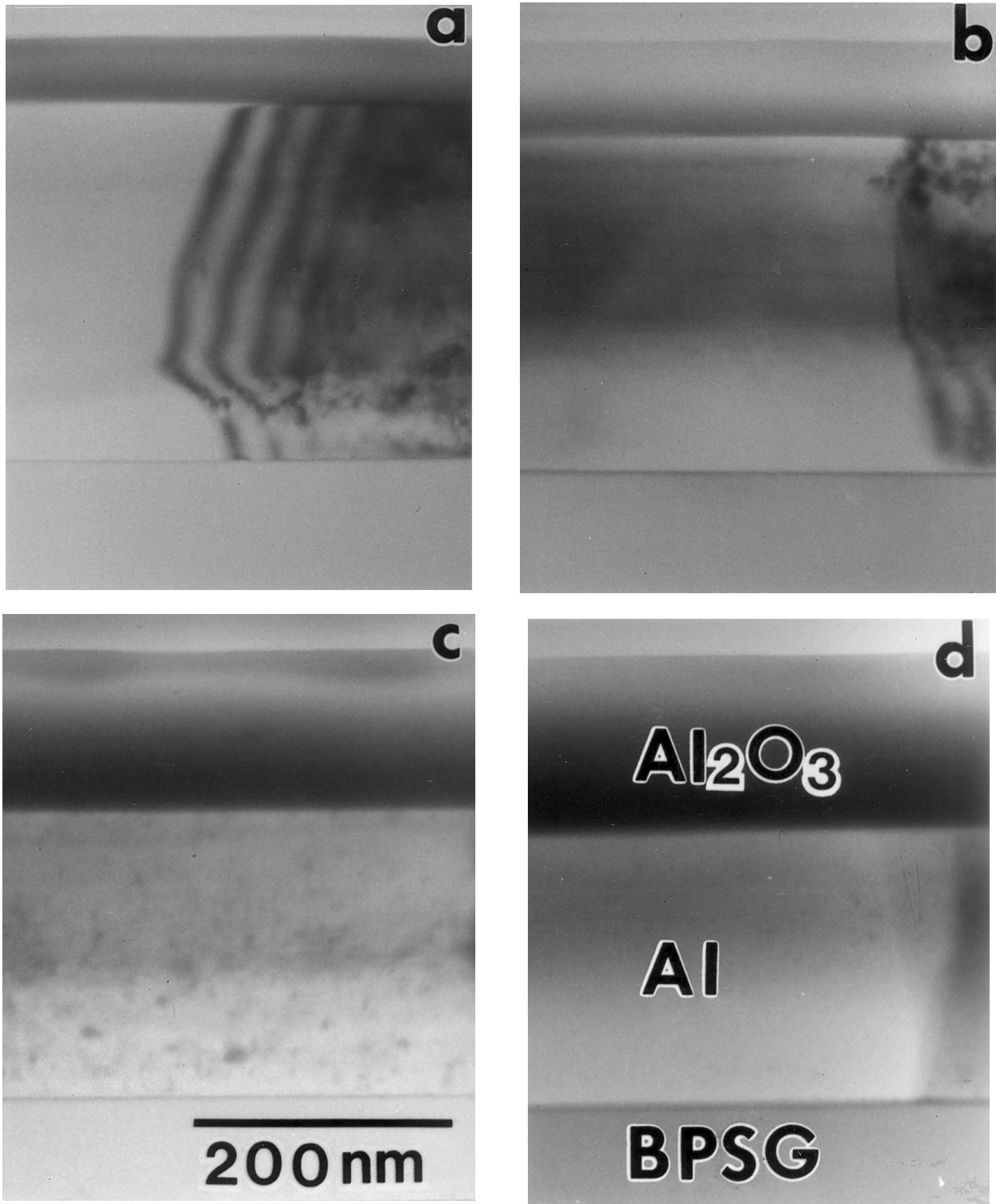
Figure 1 Cross-sectional TEM micrographs showing the microstructure of the Al$_2$O$_3$ films anodized for (a) 3.5 min; (b) 5 min; (c) 12 min; (d) 30 min.

films formed after anodizing for 210, 300, 720 and 1800 s, respectively. Different anodizing time apparently has little effect on the structure and morphology of the oxide films, except that the film thickness is increased with increasing anodizing time. The oxide films are amorphous and practically free of pinholes, voids, and grain boundaries. The uniformity of the oxide layer is excellent as can be seen clearly in Fig. 1. Fig. 2 shows the oxide thickness as a function of anodizing time. It is worth pointing out that in order to eliminate any error in the thickness

measurement, the TEM samples were tilted such that the ⟨1 1 0⟩ zone axis of the substrate silicon is aligned to the incident beam direction. This ensures that the oxide layers shown in Fig. 1 are viewed in the end-on fashion. Also, the magnifications of the TEM micrographs were calibrated against a standard sample. The dashed line in Fig. 2 marks the time when the anodizing is switched from the constant current mode to the constant voltage mode. The slope of the curve shows that the anodic oxide growth rate is 0.27 nm/s initially under a constant
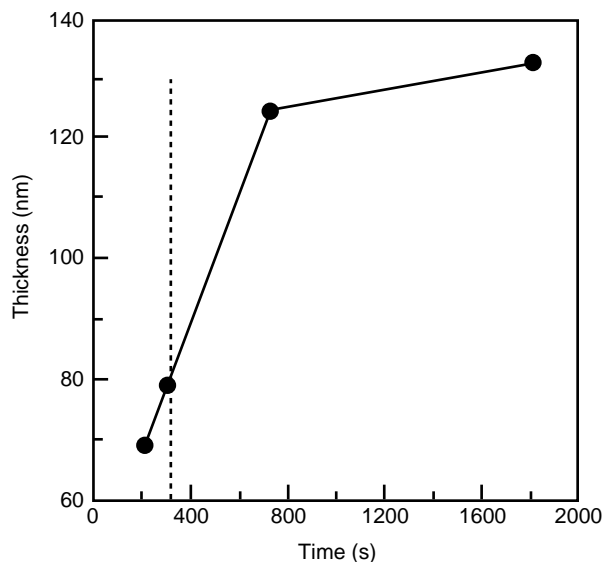
Figure 2 Variation of anodic oxide thickness with reaction time during anodizing.

Figure 3 Variation of refractive index with the anodic oxide film thickness: 2d2 anodic (this work); -- n -- dry O₂/250 8C; —s— Wet O₂; -- 3 -- Wet O₂/100 8C.

current density of 0.4 mA/cm². This growth rate is maintained well into the constant voltage regime and gradually drops off to 0.009 nm/s after the film thickness reaches 125 nm.

Utilizing the thickness value obtained by the TEM measurements with the ellipsometry data the refractive indices of the films were determined. Fig. 3 shows the variation of refractive index with anodic oxide film thickness. Similar data reported by Hoffman and Leibowitz [15] for reactively electron beam evaporated Al_2O_3 films are also included in the figure for comparison. The refractive indices of our anodic Al_2O_3 films vary from 1.48 to 1.67, increasing with film thickness. Fig. 3 reveals that for thicker films (^ 110 nm) the refractive indices of the anodic Al_2O_3 films are similar to those of the e-beam evaporated Al_2O_3 films; but thinner anodic oxide films exhibit lower refractive indices than the e-beam evaporated oxide films. Also, when the oxide film is thin, the refractive index shows large scatter depending significantly on the deposition method. On the other hand, thicker films show much less process dependence so that the four groups of data seem to fall more closely on the same line in Fig. 3.
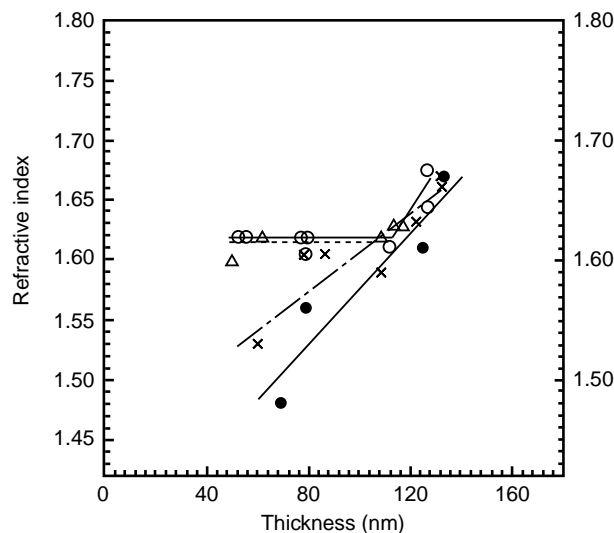
Hoffman and Leibowitz [15] had explained the higher indices of refraction for the dry oxygen evaporated Al_2O_3 films over the wet oxygen evaporated Al_2O_3 films in terms of the higher density of the former films than the latter. The variation of nonstoichiometry [18] and the densification of the anodic film under the effects of anodizing voltage and current [19] may be responsible for the increase of refractive index with film thickness. In Table I the refractive indices of relatively thick (. 120 nm) anodic Al_2O_3 oxide films formed in various electrolytes are compared. It shows that, except for one study, the refractive index of anodic alumina generally falls within a narrow range of 1.62 to 1.70 over a thickness range of 120 to 4700 nm, and the value seems to be insensitive to the electrolyte used for anodizing. For comparison, the refractive index of Al_2O_3 films prepared by other (non-anodic) techniques are listed in Table II. Generally speaking, these films show much larger scattering in refractive index, which probably reflects the process-dependent variation in film quality. The refractive index of thin Al_2O_3 films is lower than 1.76, the refractive index reported for bulk alumina

TABLE I Refractive index of anodic Al_2O_3 films

Electrolyte	Thickness (nm)	Refractive index n	Measurement method	Reference
AGW	133	1.67	Ellipsometry	This work
AGW	120	1.62	Ellipsometry	[21]
Ammonium pentaborate	400	1.65	Ellipsometry	[22]
Ammonium pentaborate ethylene	400	1.67	Ellipsometry	[22]
Ammonium tartrate	91	1.71–1.75	Ellipsometry	[7]
Ammonium tetraborate	402	1.66	Spectrophotometry	[13]
Oxalic acid	1300–4700	1.66–1.70	Photoluminescence	[14]
Sulphuric acid	350	1.63	Ellipsometry	[23]
Tartaric acid	150–200	1.62	Ellipsometry	[16]

TABLE II Refractive index of non-anodic Al_2O_3 films

Film deposition method	Thickness (nm)	Refractive index (n)	Measurement method	Reference
Activated reactive evaporation	160	1.61	Ellipsometry	[24]
CVD	–	1.62–1.71	Ellipsometry	[25]
E-beam evaporation	50–140	1.55–1.72	Ellipsometry	[15]
E-beam evaporation	130–450	1.65	Ellipsometry	[26]
E-beam evaporation	100	1.67	Interferometry	[27]
Laser deposition	110	1.63	Ellipsometry	[28]
Reactive cosputtering	–	1.65	Ellipsometry	[29]
Reactive ion sputtering	–	1.65	Ellipsometry	[30]
Reactive magnetron sputtering	100	1.65	Ellipsometry	[31]
RF magnetron sputtering	60	1.61–1.62	–	[32]
RF-sputtering	138–1650	1.46–1.69	Ellipsometry	[33]
RF-sputtering	500	1.55–1.65	Spectrophotometry	[34]
RF-sputtering	–	1.59–1.76	Ellipsometry	[35]
RF-sputtering	250	1.66	Ellipsometry	[28]
S-gun magnetron sputtering	100	1.52–1.70	Ellipsometry	[36]

[20]. The higher refractive index for the bulk alumina is expected because of its higher density of 3.96 g/cm^3 [20] relative to 3.1 g/cm^3 for anodic Al_2O_3 [11] and 2.2 to 3.9 g/cm^3 for sputtered Al_2O_3 [35].

The refractive index of anodic aluminium oxide layers formed on sputtered thin Al films increases from 1.48 to 1.67 as the film thickness is increased from 70 to 133 nm. Thicker anodic oxide films (^ 110 nm) exhibit comparable refractive indices to e-beam evaporated oxide films, but thinner (, 110 nm) anodic films have lower refractive indices than the evaporated films. The variation in refraction index may be due to the change in non-stoichiometry and density of the anodic films.

Acknowledgements

References

1. N. M. NAHAR, G. H. MO and A. IGNATIEV, *Thin Solid Films* **172** (1989) 19.
2. J. P. SEGUAD, B. DREVILLON, E. PASCUAL, R. OSSIKOVSKI, G. MONNIER and L. RIMBOURG, *ibid.* **234** (1993) 503.
3. H. YAMAMOTO, H. MATSUMARU, K. SHIRAHASHI, M. NAKATANI, A. SASANO, N. KONISHI, K. TSUTSUI and T. TSUKADA, *Technical Digest, 1990 IEEE IEDM* (1990) 851.
4. T. SUNATA, T. YUKAWA, K. MIYAKE, Y. MATSUSHITA, Y. MURAKAMI, Y. UGAI, J. TAMAMURA and S. AOKI, *IEEE Trans. Electron Devices* **ED-33** (1986) 1212.
5. R. L. CHIU, P. H. CHANG and C. H. TUNG, *J. Electrochem. Soc.* **142** (1995) 525.
6. *Idem.*, *Thin Solid Films* **260** (1995) 47.
7. K. OZAWA, K. MIYAZAKI and T. MAJIMA, *J. Electrochem. Soc.* **141** (1994) 1325.
8. H. H. STREHBLOW and C. J. DOHERTY, *ibid.* **125** (1978) 30.
9. H. H. STREHBLOW, C. M. MELLIAR-SMITH and W. M AUGUSTYNIAK, *ibid.* **125** (1978) 915.
10. K. SHIMIZU, S. TAJIMA, G. E. THOMPSON and G. C. WOOD, *Electrochimica Acta* **25** (1980) 1481.
11. M. M. LOHRENGEL, *Mater. Sci. Engng.* **R11** (1993) 243.
12. S. S. SO, *Surface Science* **56** (1976) 97.
13. G. F. PASTORE, *Thin Solid Films* **123** (1985) 9.
14. LJ. D. ZEKOVIC, V. V. UROSEVIC and B. R. JOVANIC, *ibid.* **139** (1986) 109.
15. D. HOFFMAN and D. LEIBOWITZ, *J. Vac. Sci. Technol.* **8** (1971) 107.
16. C. J. DELL'OCA, *Thin Solid Films* **26** (1975) 371.
17. P. H. CHANG, H. Y. LIU, J. A. KEENAN and J. M. ANTHONY, *J. Appl. Phys.* **62** (1987) 2485.
18. P. SKELDON, K. SHIMIZU, G. E. THOMPSON and G. C. WOOD, *Thin Solid Films* **123** (1985) 127.
19. G. A. HUTCHINS and C. T. CHEN, *J. Electrochem. Soc.* **133** (1986) 1332.
20. W. D. KINGERY, H. K. BOWEN, D. R. UHLMANN, "Introduction to ceramics", 2nd Edn (John Wiley & Sons, Singapore, 1991) pp. 596, 662 and 654.
21. H. HASEGAWA, H. YAMAMOTO, S. ARIMOTO and H. OHNO, in "Amorphous semiconductor technologies & devices", edited by Y. Hamakawa (Ohmsha, Ltd., Tokyo, 1984) p. 252.
22. R. M. GOLDSTEIN, R. J. LEDERICH and F. W. LEONHARD, *J. Electrochem. Soc.* **117** (1970) 503.
23. R. KOTZ, B. SCHNYDER and C. BARBERO, *Thin Solid Films* **233** (1993) 63.
24. J. VANFLETEREN and A. VAN CALSTER, *ibid.* **139** (1986) 89.
25. J. F. FAN, K. TOYODA, *Jpn. J. Appl. Phys.* **32** (1993) L1349.
26. P. CHINDAUDOM, K. VEDAM, *Thin Solid Films* **234** (1993) 439.
27. W. M. GOSNEY, R. S. MULLER, *ibid.* **14** (1972) 255.
28. R. SOLANKI, W. H. RITCHIE and G. J. COLLINS, *Appl. Phys. Lett.* **43** (1983) 454.
29. A. BELKIND, E. EZELL, W. GERRISTEAD, Z. ORBAN, P. RAFALKO, D. DOW, J. FELTS and R. LAIRD, *J. Vac. Sci. Technol.* **A9** (1991) 530.
30. A. B. HARKER and J. F. DENATALE, *Thin Solid Films* **168** (1989) 185.

31. G. ESTE and W. D. WESTWOOD, *J. Vac. Sci. Technol.* **A2** (1984) 1238.
32. C. DESHPANDEY, *Thin Solid Films* **96** (1982) 265.
33. R. S. NOWICKI, *J. Vac. Sci. Technol.* **14** (1977) 127.
34. C. A. T. SALAMA, *J. Electrochem. Soc.* **117** (1970) 913.
35. K. K. SHIH and D. B. DOVE, *J. Vac. Sci. Technol.* **A12** (1994) 321.
36. P. J. CLARKE, *ibid.* **A12** (1994) 594.