Proceedings of the Estonian Academy of Sciences,
2019, **68**, 2, 126–130
https://doi.org/10.3176/proc.2019.2.01
Available online at www.eap.ee/proceedings

MATERIALS
ENGINEERING

Mechanical and tribological properties of 100-nm thick alumina films prepared by atomic layer deposition on Si(100) substrates

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Received 20 December 2018, accepted 11 February 2019, available online 28 March 2019

Abstract. The study investigates mechanical and tribological properties of alumina (Al_2O_3) films prepared on Si(100) substrates. The 100-nm thick films were deposited by atomic layer deposition. Nanoindentation and nano-scratch tests were performed with Berkovich and sphero-conical diamond indenters, respectively. Energy-dispersive X-ray spectroscopy and optical and scanning electron microscopy were used to analyse the surface morphology and chemical composition of the thin films. X-ray diffraction was used to characterize their crystal structure. Crystallization was found to start at 1100 °C after 3 hours of annealing. The hardness and tribological properties of the alumina films were influenced by the substrate in nanoindentation and nano-scratch tests. Within the relatively low load range (5–50 mN), the coefficient of friction of Si and alumina against diamond depended on the load, most likely due to a change in the elastic/plastic deformation behaviour within the Si substrate.

Key words: nanoindentation, alumina oxide thin films, atomic layer deposition, nano-scratch, deformation.

1. INTRODUCTION

Alumina films are an important technological material used for chemical and mechanical protection of engineering components [1] and in the manufacturing of optical devices and micro-electromechanical systems. Preparation of patterned alumina films is an important aspect of modern technology to study the influence of surface textures on friction and wear [2].

Atomic layer deposition (ALD) is widely used for the preparation of alumina films [3]. Nanoindentation and nano-scratching are well-known methods to determine the mechanical properties of thin films. The nano-hardness of alumina films can vary between 6 and 12 GPa [4,5]. However, there is a lack of investigations of mechanical properties of thin alumina films by the nano-scratch method.

This study focuses on mechanical and tribological properties (within 0.2–400 mN of load) of 100-nm thick alumina films deposited on Si(100).

2. EXPERIMENTAL METHODS

The alumina thin films of 100-nm thickness were prepared on Si(100) substrates by the ALD method with subsequent annealing. The deposition temperature was 300 °C. The temperature and duration of annealing for different samples are shown in Table 1.

The nanoindentation tests were carried out by means of a nano-mechanical testing system (NanoTest, Micro Materials Ltd.) using a diamond Berkovich indenter.

The applied loads were varied between 0.2 and 0.45 mN with the increment of 0.05 mN. The nano-indentation was performed with a series of 10 indentations at each load on each sample. The mechanical properties

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Table 1. Post-deposition annealing parameters of films

	Samples					
	1	2	3	4	5	6
Temperature (°C)	25	500	700	900	1100	1100
Time (h)	–	1	1	1	2	3

Table 2. Parameters for nano-scratch tests for Si(100) and Al_2O_3/Si(100) samples

Peak load (mN)	Loading rate, dL/dt (mN/s)	Scan speed, dx/dt (µm/s)	dL/dx (mN/µm)
5, 7, 10, 20, 50, 100, 200, 300, 400	5	2	2.5

of the Si substrate and alumina films, such as the hardness and elastic modulus, were determined by the Oliver–Pharr method [6]. The nano-scratch tests were performed using a sphero-conical diamond indenter with a radius of 5 µm (the tests details are listed in Table 2).

The friction force (F_x) and friction coefficient (COF) were the parameters of interest for nano-scratch tests. The surfaces of samples after the scratch tests were examined by optical microscopy.

3. RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM) images taken of the Al_2O_3 films are shown in Fig. 1. The as-deposited film (sample 1 in Table 1) has a uniform smooth layer (Fig. 1a). A similar surface morphology was observed after annealing at 500, 700, and 900 °C. The holes within the oxide layer (sample 6) can be seen in the SEM image after annealing at 1100 °C for 3 h (Fig. 1b). This demonstrates how the patterned alumina films can be prepared.

SEM images taken in the backscattered-electron (BSE) mode are shown in Fig. 2a and Fig. 2b along with the energy-dispersive X-ray spectroscopy (EDS) patterns. The spectrum taken within the hole shows a relatively strong Si signal, indicating the peeling of the film after annealing at 1100 °C for 3 h in comparison with the spectrum corresponding to the pristine alumina film surface, which possesses a strong Al peak. The X-ray diffraction (XRD) patterns taken on samples 5 and 6 indicate the formation of a crystalline structure after 3 h of annealing (Fig. 2c). The study of the literature suggests that most likely multiphase alumina was formed [7]. The structure of samples 1–5 was amorphous.

The nanohardness and Young's modulus of the Si(100) substrate were in the range of 10.6–13.2 GPa

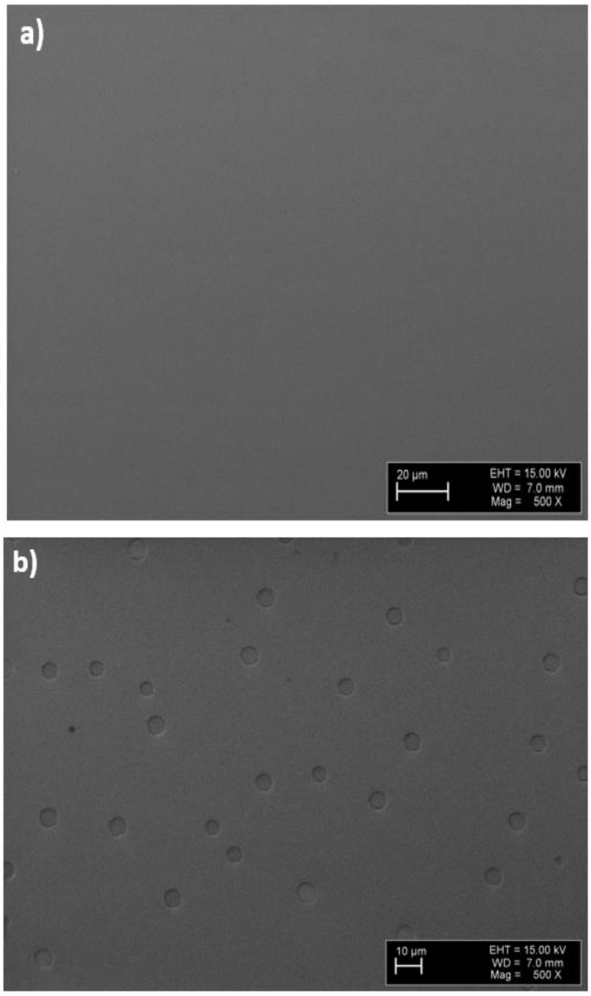

Fig. 1. Surface morphology of Al_2O_3 films: (a) as-deposited and (b) annealed at 1100 °C for 3 h.

and 142–169 GPa, respectively, which is in good agreement with the literature [8]. The hardness and Young's modulus of as-deposited and annealed at 500, 700, 900, and 1100 °C alumina films were in the range of 10–13 GPa and 150–190 GPa; thus the Si(100) substrate influenced the properties of the alumina films (Table 3).

The scratch test on the Si(100) substrate, illustrated in Fig. 3, was performed at the peak load of 200 mN. The results of the scratch test are in good agreement with the literature [9]. The main transitions on the Si substrate are as follows: L_y – onset of non-elastic deformation, Lc_1 – pop-in observed by an accompanied change in the colour of the scratch track, and Lc_2 – prominent chipping observed at the edges of the track.

The behaviour of alumina film (sample 1) under the peak load of 200 mN is shown in Fig. 4a. Chipping starts at $Lc_2 = 78$ mN. The response of Al_2O_3 film

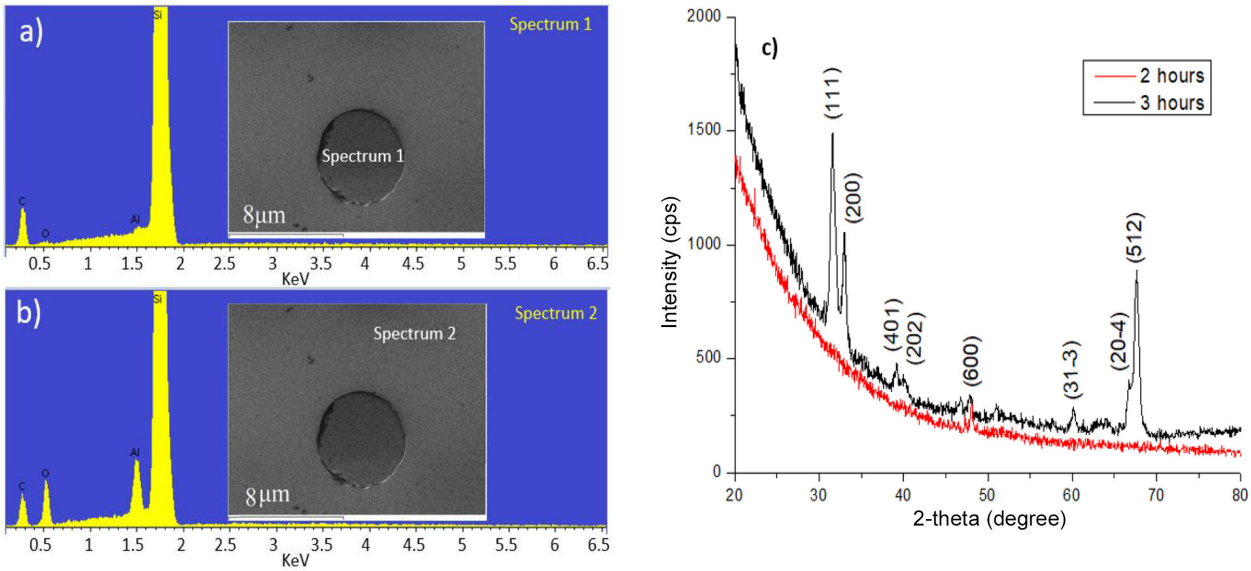

Fig. 2. BSE images and EDS spectra taken on sample 6: (a) within the hole, (b) on the film surface, and (c) XRD pattern after 2 and 3 hours of annealing at 1100 °C.

Table 3. Hardness (GPa) and Young's modulus (GPa) measured on the Si(100) and alumina films

	Si	1	2	3	4	5	6
Nanohardness	11.9 ± 1.3	10.2 ± 1	10.5 ± 1	9.9 ± 0.9	10.4 ± 0.9	12.6 ± 1.4	12 ± 0.9
Young's modulus	154.4 ± 12.9	172.3 ± 19.4	178.1 ± 19	171.0 ± 15	173.8 ± 16.7	169.6 ± 20.6	173.9 ± 20

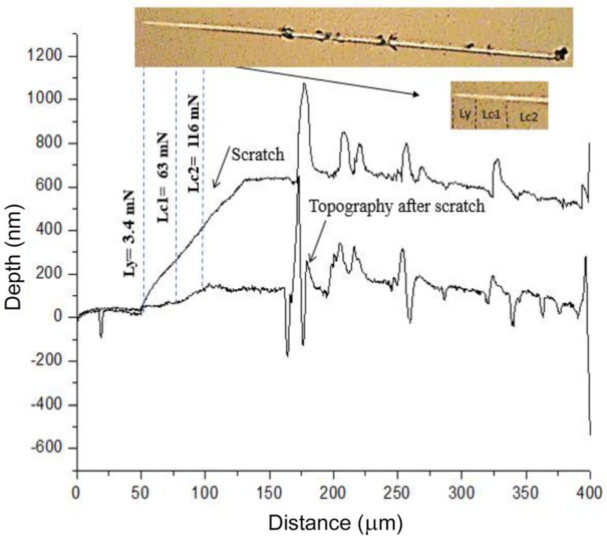

Fig. 3. Nano-scratch test on the Si substrate at the peak load of 200 mN.

(sample 6) at the peak load of 200 mN is shown in Fig. 4b; no clear Lc_1 transition was observed. Chipping starts at $Lc_2 = 89$ mN. There is a good correlation with the value of 63 mN (Lc_1) observed on Si(100), which shows the influence of substrate on the properties of alumina films, i.e. when severe deformation starts within the Si substrate.

Figure 5a shows that there is a correlation between the normal load and friction force. According to Amontons' law of friction, the friction force is directly proportional to the normal load $F_x = \mu N$, where F_x denotes frictional (tangential) force, N is normal load, and μ is the coefficient of friction. The COF is the coefficient of proportionality and it is independent of load [10,11]. Figure 5b shows COF versus normal load. It should be noted that the COF value increased for alumina and Si within stage 1, which is a disagreement with Amontons' law of friction. According to data shown in Figs 3 and 4, the elastic deformation as well as plastic deformation dominated in this stage. Most likely, the COF value changed due to the mainly continuous change of the elastic–plastic behaviour of Si. Therefore, contact conditions between the indenter and sample surface changed continuously as well. However, for stage 2, the COF values were nearly constant; such behaviour shows agreement with the above-mentioned law of friction.

The plastic deformation and wear (chipping) were dominant processes for stage 2 (Figs 3 and 4). The COF

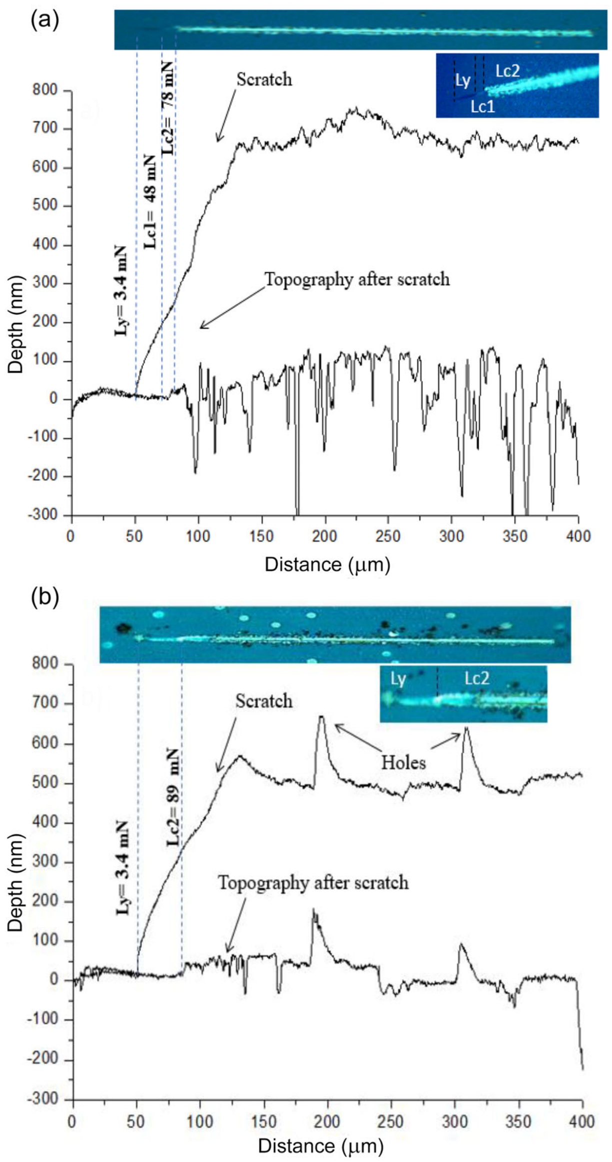

Fig. 4. Nano-scratch tests on alumina along with traces taken by means of optical microscopy: (a) as-deposited sample 1 and (b) sample 6.

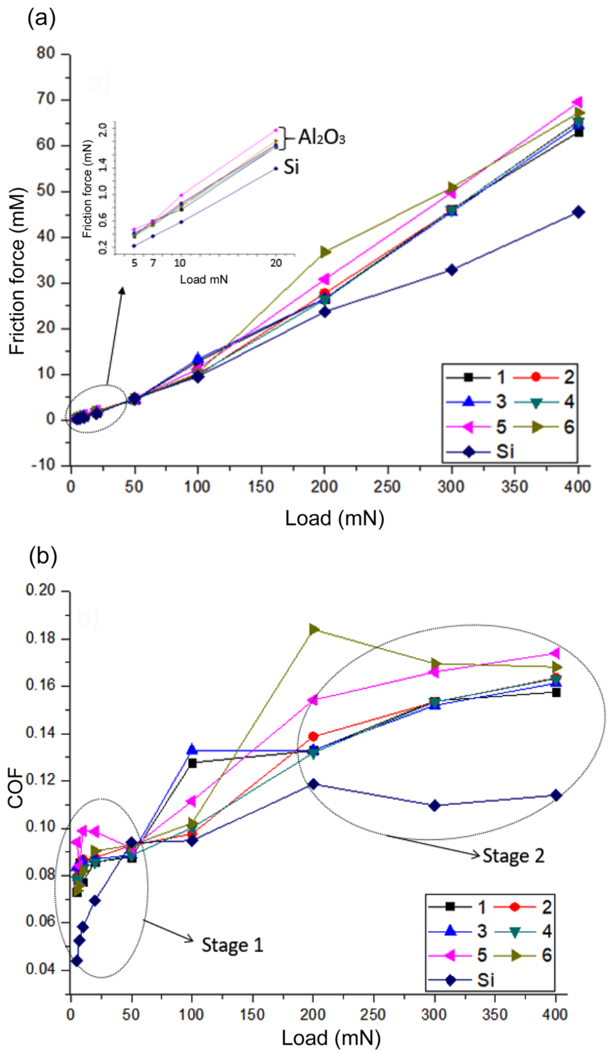

Fig. 5. Friction parameters at nano-scratch tests: (a) friction force and (b) COF versus load curves.

for Si(100) substrate within the load range of 200–400 mN was 0.1, which is in good agreement with the literature [12]. The dependence of the COF values on the load between alumina and diamond in sliding tests was observed in previous studies as well [13]. There is a clear difference between COF values for alumina and Si for low loads (5–20 mN), where the elastic–plastic deformation dominated (Figs 3 and 4). In other words, in spite of the strong influence of the substrate observed in nanoindentation tests even for the lower loads (up to 0.45 mN), see discussion above, the tribological properties of alumina differed from those for the Si substrate in nano-scratch tests. The difference in COF values for higher loads (200–400 mN), where severe wear was the dominant process, probably means that the alumina films were not fully delaminated from Si substrates.

4. CONCLUSIONS

Nanoindentation and nano-scratch tests were performed to evaluate the mechanical and tribological properties of thin alumina films deposited on Si(100) substrates. The measurements of hardness and Young's modulus of Al_2O_3 thin films were influenced by the Si substrate. After annealing at 1100 °C, formation of holes within Al_2O_3 films was observed. Disagreement with Amontons' law of friction was found for the loads in the range of 5–20 mN, which probably corresponds to a continuous change from elastic to plastic deformations within the Si substrate. However, for the higher loads (200–400 mN), where the wear is the dominant process, a good agreement was found with Amontons' law.

ACKNOWLEDGEMENTS

This study was financially supported by the Estonian Ministry of Education and Research under target financing project IUT 19-29 'Multi-scale structured ceramic-based composites for extreme applications' and was partially supported by the European Regional Development Fund project 'Emerging orders in quantum and nanomaterials' (TK134), Estonian Academy of Sciences (SLTFYPROF), and Estonian Research Agency (PRG4).

Special thanks to Taivo Jõgiaas, PhD (Laboratory of Technology Thin Film, University of Tartu, Estonia), for supplying the samples and constructive reviewing of the manuscript.

The publication costs of this article were covered by the Estonian Academy of Sciences.

REFERENCES

1. Li, X., Diao, D., and Bhushan, B. Fracture mechanisms of thin amorphous carbon films in nanoindentation. *Acta Mater.*, 1997, **45**, 4453–4461.
2. Gachot, C., Rosenkranz, A., Hsu, S. M., and Costa, H. L. A critical assessment of surface texturing for friction and wear improvement. *Wear*, 2017, **372**, 21–41.
3. Leskelä, M. and Ritala, M. Atomic layer deposition (ALD): from precursors to thin film structures. *Thin Solid Films*, 2002, **409**(1), 138–146.
4. Miller, D. C., Foster, R. R., Jen, S. H., Bertrand, J. A., Cunningham, S. J., Morris, A. S., et al. Thermo-mechanical properties of alumina films created using the atomic layer deposition technique. *Sensor. Actuat. A-Phys.*, 2010, **164**, 58–67.
5. Tripp, M. K., Stampfer, C., Miller, D. C., Helbling, T., Herrmann, C. F., Hierold, C., et al. The mechanical properties of atomic layer deposited alumina for use in micro- and nano-electromechanical systems. *Sensor. Actuat. A-Phys.*, 2006, **130**, 419–429.
6. Oliver, W. C. and Pharr, G. M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.*, 1992, **7**, 1564–1583.
7. Nayar, P., Khanna, A., Kabiraj, D., Abhilash, S. R., Beake, B. D., Losset, Y., and Chen, B. Structural, optical and mechanical properties of amorphous and crystalline alumina thin films. *Thin Solid Films*, 2014, **568**, 19–24.
8. Boyd, E. J. and Uttamchandani, D. Measurement of the anisotropy of Young's modulus in single-crystal silicon. *J. Microelectromech. S.*, 2012, **21**, 243–249.
9. Beake, B. D., Liskiewicz, T. W., and Smith, J. F. Deformation of Si(100) in spherical contacts – comparison of nano-fretting and nano-scratch tests with nano-indentation. *Surf. Coat. Tech.*, 2011, **206**, 1921–1926.
10. Wong, M. S., Meilunas, R., Ong, T. P., and Chang, R. P. H. Tribological properties of diamond films grown by plasma-enhanced chemical vapor deposition. *Appl. Phys. Lett.*, 1989, **54**, 2006–2008.
11. Bhushan, B., Subramaniam, V. V., Malshe, A., Gupta, B. K., and Ruan, J. Tribological properties of polished diamond films. *J. Appl. Phys.*, 1993, **74**, 4174–4180.
12. Bhushan, B. and Li, X. Micromechanical and tribological characterization of doped single-crystal silicon and polysilicon films for microelectromechanical systems devices. *J. Mater. Res.*, 1997, **12**, 54–63.
13. Yurkov, A. L., Skvortsov, V. N., Buyanovsky, I. A., and Matvievsky, R. M. Sliding friction of diamond on steel, sapphire, alumina and fused silica with and without lubricants. *J. Mater. Sci. Lett.*, 1997, **16**, 1370–1374.

Si(100) substraatidele aatomkihtsadestamisel valmistatud 100 nm paksusega Al_2O_3 kilede mehaanilised ja triboloogilised omadused

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Si(100) substraatidele sadestatud õhukeste alumiiniumoksiidi pinnete mehaaniliste ja triboloogiliste omaduste hindamiseks viidi läbi nanoindentatsiooni- ning nanokriimustuste testid. Si substraat mõjub tema pinnale sadestatud õhukeste Al_2O_3 pinnete kõvadusele ja elastsusmooduli väärtusele. Pärast kuumutamist 1100 °C juures täheldati aukude moodustumist Al_2O_3 pinde sees. Lahknevus Amontonsi hõõrdumisseadusega leiti koormuste vahemikust 5–20 mN, mis võib tõenäoliselt vastata pidevale üleminekule elastselt deformatsioonilt plastsele deformatsioonile Si substraadis. Suuremate koormuste (200–400 mN) puhul, kus kulumine on domineeriv protsess, leiti Amontonsi seadusega hea vastavus.