ISSN 1995-0780, Nanotechnologies in Russia, 2018, Vol. 13, Nos. 9–10, pp. 502–507. © Pleiades Publishing, Ltd., 2018.
Original Russian Text ©A.A. Dedkova, N.A. Dyuzhev, V.Yu. Kireev, I.E. Klemente, A.V. Myakon'kikh, K.V. Rudenko, 2018, published in Rossiiskie Nanotekhnologii, 2018, Vol. 13, Nos. 9–10.

FUNCTIONAL NANOMATERIALS

# Study of the Effect of Laser Radiation on the Parameters of Alumina Films Formed by Atomic Layer Deposition

**A. A. Dedkova**[a], **N. A. Dyuzhev**[a], **V. Yu. Kireev**[a,*], **I. E. Klemente**[b],
**A. V. Myakon'kikh**[b], **and K. V. Rudenko**[b]
[a] *National Research University of Electronic Technology, Moscow, Zelenograd, 124498 Russia*
[b] *Valiev Institute of Physics and Technology, Russian Academy of Sciences, Moscow, 117218 Russia*
**e-mail: valerikireev@mail.ru*

Received May 7, 2018; accepted October 28, 2018

**Abstract**—The effect of laser radiation with a wavelength of 970 nm and a power density of 0.29–2.10 W/cm$^2$ on the process of atomic layer deposition of alumina films from precursors (trimethylaluminium + water vapor) is studied. Laser irradiation is performed at the stages of reactor purging after the introduction of precursors. The results of a comprehensive analysis involving spectral ellipsometry, atomic force microscopy, X-ray diffractometry, and secondary-ion mass spectrometry have revealed that laser irradiation (i) does not alter the rate of deposition of alumina films onto silicon slices; (ii) does not alter the surface relief (roughness) of alumina films; (iii) does not alter the depth profile of the chemical composition of alumina films; (iv) reduces the average density of irradiated regions of alumina films by 5–10% relative to the density of nonirradiated regions.

**DOI:** 10.1134/S199507801805004X

## INTRODUCTION

The processes of atomic layer chemical vapor deposition (AL CVD) or atomic layer deposition (ALD) [1] based on molecular assembly or molecular layering belong to the group of CVD processes with discrete feeding of reagents, which are commonly called precursors [2]. The ALD mechanism relies on the multiple repetition of cyclic (discrete) self-terminating chemical reactions between the precursor molecules on the substrate surface [3–5].

The method of molecular assembly or molecular layering was developed by V.B. Aleskovskii and his colleagues at the Faculty of Chemistry of the Lensoviet Leningrad Institute of Technology in the early 1950s [6–8].

However, the results of these studies have not been published in international academic journals, and the author certificates were classified. This is the reason why Finnish scientists, led by T. Suntola, who filed the first Finnish ALD patent in 1974 and the first American patent in 1977, are considered in English-speaking countries to be the founders of ALD [9].

A typical ALD process may be broken down into consecutive stages of feeding of precursors. These are separated temporally by periods of reactor purging with an inert gas, which removes the remaining precursors and reactive reaction products. At the first deposition stage, the first precursor is chemisorbed on the substrate surface to the point when surface states (adsorption centers) become saturated completely.

The second deposition stage involves reactor purging with an inert gas and the removal of molecules of the first precursor. At the third stage, the second precursor is fed into the reactor. This precursor reacts with the adsorbed layer of the first precursor to form the desired monolayer film and volatile byproducts. At the fourth stage, the reactor is purged with an inert gas, and unreacted molecules of the second precursor and the formed volatile byproducts are removed [1, 4].

This cycle is repeated many times, which results in a slow layer-by-layer growth of a dense film on the substrate surface. The film thickness is adjusted by setting the necessary number of reaction cycles. Since self-stopping deposition reactions in ALD processes are governed by the adsorption capacity of the substrate surface with respect to the precursor, small variations (deviations) of process parameters such as the precursor flow rates, the pressure in the reactor, and the substrate temperature do not alter the technological characteristics of films in any appreciable way.

Therefore, ALD films are exceptionally uniform in thickness with high degrees of conformity of the relief coating (Table 1) [5]. ALD precursors (reagents) for almost all metal, semiconductor, and dielectric films used in microelectronics are now available [4].

ALD films are characterized by low levels of mechanical stress and a lack of pores. In addition, ALD reactors make it easy to deposit successively several films of different materials with precision control of their thicknesses [4]. There is no doubt that ALD will be the method of choice for the fabrication of

**Table 1.** Comparison of characteristics of the processes of physical vapor deposition (PVD), chemical vapor deposition (CVD) with continuous reagent feeding, and atomic layer deposition (ALD) [5]

| Parameter | PVD | CVD | ALD |
|---|---|---|---|
| Typical deposition rate $v_d$, nm/min | 100–1000 | 10–100 | 0.1–1.0 |
| Typical thickness $d$ of deposited films, nm | 20–1500 | 10–1300 | 1.0–50 |
| Typical uniformity $R$ of the deposition (coating) rate, % | >95 | >97.5 | >99 |
| Accuracy of temporal control over the film thickness in the process of deposition (coating), nm | ±5.0 | ±1.0 | ±0.01 |
| Degree of conformity of the relief coating $\alpha_c$, % (relief aspect ratio $AR$) | 50 $AR = 10$ | 90 $AR = 10$ | 100 $AR = 60$ |
| Mechanism of film deposition | Physical sputtering | Gas-phase chemical reactions | Chemical reactions on the substrate surface |
| Degree of influence of process parameters on the technological characteristics of films | Very strong influence | Strong influence | Weak influence |
| Geometry size $L$ at which quality coating of the side walls of contact openings is provided, nm | >100 | 90–65 | <10 |

(1) Degree of conformity of the step (topological relief) coating $\alpha_c = (s/z) \times 100$, where $s$ and $z$ are the thicknesses of the thinnest and thickest regions of the deposited film on the side of a step. (2) The ratios of the depth of a groove to its width, the depth of an aperture to its diameter, and the height of a step to its width are called aspect ratios ($AR$).

microelectronic devices and systems with nanometer-scale elements with the use of nanotechnology [1, 4]. ALD processes are also indispensable in the fabrication of ultrathin barrier metal and dielectric layers in biosensors, biocompatible prostheses, supercapacitors, and solar cells [10–12].

The primary disadvantage of ALD processes is the low deposition rate, which limits their industrial use to films with a thickness of ≤50 nm. The results of theoretical analysis of the ALD mechanism [13–15] suggest that this rate may be increased by

(i) enhancing the rate of chemical reactions at the stages of precursor (reagent) feeding via laser activation of the substrate surface;

(ii) shortening the stages of reactor purging with an inert gas by accelerating the processes of desorption of unreacted precursors and volatile reaction products via the laser activation of the substrate surface.

However, the rate of the chemical reaction between precursors 1 and 2, which results in the production of molecules of the film material, increases both in the irradiated substrate region and in the reactor volume through which the laser beam passes: laser radiation may desorb the first precursor (e.g., water molecules) chemisorbed on the substrate surface, and these desorbed molecules may then react, under the influence of laser radiation, with molecules of the second precursor (TMA) within the reactor and produce alumina particles.

Such chemical reactions reduce the density of a film and make its structure powderlike, thus rendering it useless for microelectronics [1]. If one manages to suppress bulk chemical reactions, the optical activation of surface chemical reactions provides an opportunity to perform ALD at lower temperatures. This may be critically important if the processed slice already has certain structures formed on it and plasma-enhanced ALD is not applicable due to the fact that it produces defects [4].

We have not found any data regarding the influence of laser radiation on the ALD process in the available literature. However, the adsorption and chemical reactions may be stimulated by laser irradiation [1]. It is convenient to perform such irradiation at the stages of reactor purging.

The aim of this study is to examine the possibility of adjusting the rate of ALD processes by subjecting the substrate surface with the deposited film to laser irradiation at the stages of reactor purging.

## EXPERIMENTAL

The process of ALD of alumina ($Al_2O_3$) films was studied using a FlexAL system (Oxford Instruments Plasma Technology, Great Britain; see Fig. 1). The first precursor was an organometallic compound (trimethylaluminium (TMA) $Al(CH_3)_3$). This precursor allows one to synthesize high-quality alumina films at a substrate temperature of ~300°C. TMA has a high saturated vapor pressure at room temperature, thus providing the opportunity to shorten the time of precursor feeding and purging and reduce the temperature of the precursor container in the process of deposition. Water vapor ($H_2O$) was the second precursor.

The experimental setup allows for the plasma activation of one of the gas reagents fed through inlet *6* (Fig. 1) into an inductive coupled plasma (ICP) source. A shutter occluding the plasma source for the duration of precursor feeding into the chamber was used to prevent the deposition of films onto the ceramic cylinder of the ICP source and thus avoid the possible deterioration of its characteristics. The same shutter was used to control the process of laser irradiation when the laser was operated in the continuous mode.

The setup is fitted with an automated vacuum load lock, which allows one to load and remove substrates without admitting the atmosphere into the chamber. Substrates with diameters up to 200 mm are supported. Single-crystal silicon slices KDB-12(100) 100 mm in diameter were used in the experimental study of the effect of laser radiation on the process of ALD of alumina films at the stages of reactor purging. The residual pressure in the reactor was $1.3 \times 10^{-4}$ Pa, and the temperature of the substrate supporting the processed slice was stabilized at 300°C.

An M-2000X spectral ellipsometer (J.A. Woollam Co. Inc, United States) was used to monitor the thickness of silica ($SiO_2$) and alumina ($Al_2O_3$) films and the coating uniformity. This device has the capacity to perform measurements at 479 different wavelengths from 246.3 to 999.8 nm.

The ellipsometer features two operation modes for ex situ measurements outside the ALD setup in laboratory conditions and for in situ measurements directly in the process of ALD. In ex situ measurements, the instrument is mounted on a special automated platform with a positioning table for substrates with diameters up to 200 mm. The tilt of this table may be calibrated manually. The platform is fitted with a mechanism for shifting the ellipsometer vertically with respect to the table. Ex situ measurements were performed in experiments with the spectral ellipsometer.

The thickness of the equilibrium natural oxide layer on KDB-12(100) single-crystal silicon slices 100 mm in diameter was measured using the spectral ellipsometer prior to the experiments. The determined average thickness was 2 nm.

An LSP 0.97/20 (IRE-Polyus) surgical laser with a wavelength of 970 nm and adjustable output power (1–20 W) was used to perform the laser irradiation of the surface of silicon substrates in the process of alumina deposition at the stages of reactor purging. Laser radiation was transmitted through optical port 7 (Fig. 1). The energy of laser radiation quanta at the indicated wavelength is much higher than the energy of adsorption of water molecules on the alumina surface (see below).

## RESULTS AND DISCUSSION

The general diagram of the standard process of ALD of an $Al_2O_3$ film in experiments with FlexAL is shown in Fig. 2. The alumina film on silicon slice *L3* was deposited in 200 ALD cycles in accordance with the diagram in Fig. 2 without laser irradiation of the substrate surface. Figure 3a shows the distribution of thickness of the deposited $Al_2O_3$ film (determined using the spectral ellipsometer) over the substrate surface. The average thickness of the alumina film was 16.60 ± 0.21 nm.

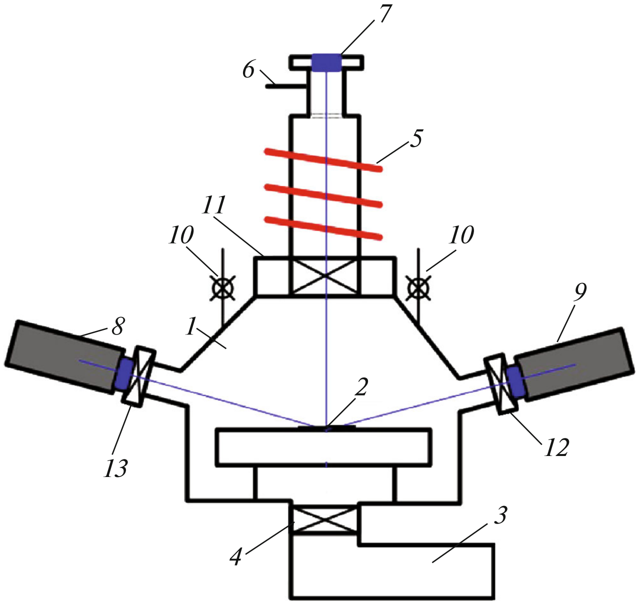

**Fig. 1.** (Color online) Diagram of the FlexAL atomic layer deposition system. Reactor chamber *1*, substrate *2* with the deposited film, turbomolecular pump line *3*, automatic pressure control valve *4*, inductor *5* of the ICP source, gas inlet *6*, optical port *7* for laser radiation, source *8* and receiver *9* of the spectral ellipsometer, precursor supply lines *10*, valve *11* for blocking off the plasma source (may be used to switch laser radiation on and off) , and optical ports *12* and *13* (with shutters) of the receiver and the source of the spectral ellipsometer are indicated.

The central region of the *L4* silicon slice with a diameter of 3 cm was irradiated for 5 s (970 nm, 0.29 W/cm$^2$) within 200 ALD cycles at the purging stages. Steps 2 and 4 in the diagram in Fig. 2 were organized as follows: 1 s (purging) + 5 s (purging and laser irradiation) + 2 s (purging) = 8 s. Figure 3b shows the distribution of thickness of the deposited $Al_2O_3$ film over the surface of sample *L4*. The average film thickness was the same (17.20 ± 0.15 nm) in irradiated and nonirradiated regions.

The central region of silicon slice *L5* with a diameter of 3 cm was irradiated for 5 s (970 nm, 2.1 W/cm$^2$) within 200 ALD cycles at the purging stages. The average film thickness was the same (17.34 ± 0.20 nm) in irradiated and nonirradiated regions.

Thus, local laser irradiation at 970 nm with different power densities at the stages of reactor purging in the process of ALD of alumina films had no appreciable effect on the deposition rate. In addition, the overall thickness of $Al_2O_3$ films deposited under local laser

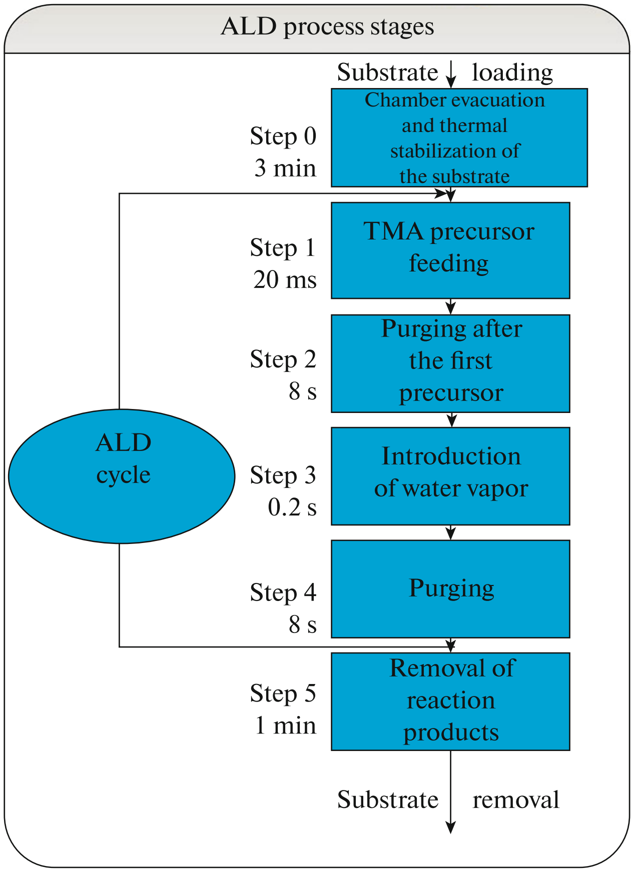

**Fig. 2.** (Color online) Diagram of the standard process of atomic layer deposition of an alumina ($Al_2O_3$) film in experiments with FlexAL. The pressure in the containers with TMA and water is set by stabilizing their temperatures at 35 and 18°C, respectively.

irradiation with various power densities differed slightly (by 0.6–0.74 nm) from that of the films deposited without irradiation. This difference may be attributed to the fact that the temperature of silicon substrates was slightly higher than the set one (300°C).

The experimental data, which suggest that laser irradiation at 970 nm has no effect on the desorption of water molecules in the process of ALD of $Al_2O_3$ films, contradict the results presented in [16], where the energy of adsorption of water molecules on the surface of an alumina layer was estimated at 1.26 eV.

Energy $\varepsilon$ of IR laser quanta with $\lambda = 970$ nm is given by [17]

$$\varepsilon = h\nu = (hc)/\lambda, \tag{1}$$

where $h$ is the Planck constant ($6.63 \times 10^{-34}$ J s), $\nu$ is the radiation frequency (Hz), and $c$ is the speed of light ($2.99 \times 10^8$ m/s).

Formula (1) yields $\varepsilon = 2.04 \times 10^{-19}$ J for our laser; since 1 eV = $1.6 \times 10^{-19}$ J, $\varepsilon = 1.28$ eV. This energy exceeds the adsorption energy of water molecules on the surface of an alumina layer [16]. If such irradiation does not affect the ALD rate, it should alter the structure and/or chemical composition of alumina films in the irradiated regions.

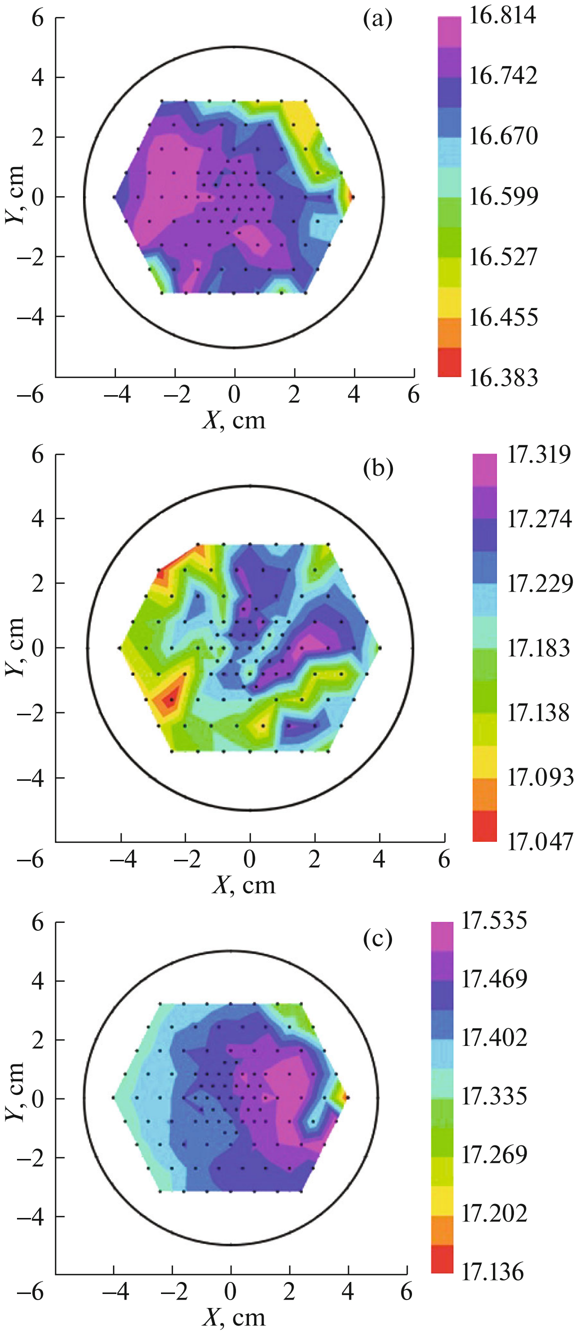

**Fig. 3.** (Color online) Distribution of the thickness (nm) of ALD $Al_2O_3$ films over the substrate surface: (a) sample *L3* without laser irradiation; (b, c) samples *L4* and *L5* with their central regions 3 cm in diameter irradiated for 5 s (970 nm) at the purging stages with a power density of 0.29 and 2.1 W/cm$^2$.

In order to verify this assertion, the irradiated and nonirradiated regions of deposited $Al_2O_3$ films on slices *L*3, *L*4, and *L*5 were studied using

**Table 2.** Average density ρ of $Al_2O_3$ films in the irradiated and nonirradiated regions of samples *L3*, *L4*, and *L5*

| Sample | $\rho(Al_2O_3)$, g/cm$^3$ |
|---|---|
| *L3* (nonirradiated slice) | 3.24 |
| *L4* (nonirradiated region) | 3.24 |
| *L4* (irradiated region) | 2.94 |
| *L5* (nonirradiated region) | 3.23 |
| *L5* (irradiated region) | 3.11 |

The average density of a stable rhombohedral α-modification of alumina (corundum) is 3.99 g/cm$^3$.

(i) a SmartLab (Rigaku, Japan) multifunctional X-ray diffractometer;

(ii) a SmartSPM (AIST-NT, Russia) scanning probe microscope;

(iii) a TOF.SIMS 5 (IONTOF, Germany) secondary-ion mass spectrometry (SIMS) system.

The X-ray patterns obtained using SmartLab were used to determine average density ρ of alumina films on the irradiated and nonirradiated regions of slices *L3*, *L4*, and *L5*. The geometry of a parallel X-ray beam with wavelength $\lambda(\mathrm{Cu}K_{\alpha 1}) = 0.15406$ nm in the 2θ scan mode with angular pitch $\Delta\theta = 0.004°$ was used. The percentage error of intensity measurements with the indicated diffractometer is ±2% at a confidence level of 0.95. The measurement results are presented in Table 2.

It can be seen that the nonirradiated alumina film has an average density of 3.24–3.23 g/cm$^3$ on all substrates, while the irradiated alumina film had an average density of 2.94 and 3.11 g/cm$^3$ on slices *L4* and *L5*, respectively. Such differences (as large as 10%) in the average density are not related to measurements errors and reflect a change in the deposition mechanism induced by laser irradiation.

We believe that the distance between aluminum or oxygen atoms in the plane parallel to the substrate surface increases under laser irradiation. This was revealed by the X-ray radiation of the diffractometer that propagated along the surface. The beam of the spectral ellipsometer, which was directed almost at a right angle to the substrate, did not expose any differences in the thickness of $Al_2O_3$ films in the irradiated and nonirradiated regions. In addition, ALD $Al_2O_3$ films synthesized on polished silicon surfaces are defect-free.

The experiments with SmartSPM did not reveal practically significant differences in thickness and relief (roughness) between the irradiated and nonirradiated regions of alumina films on samples *L4* and *L5*.

The results of SIMS analysis of the irradiated and nonirradiated regions of alumina films on substrate *L4* are presented n Fig. 4.

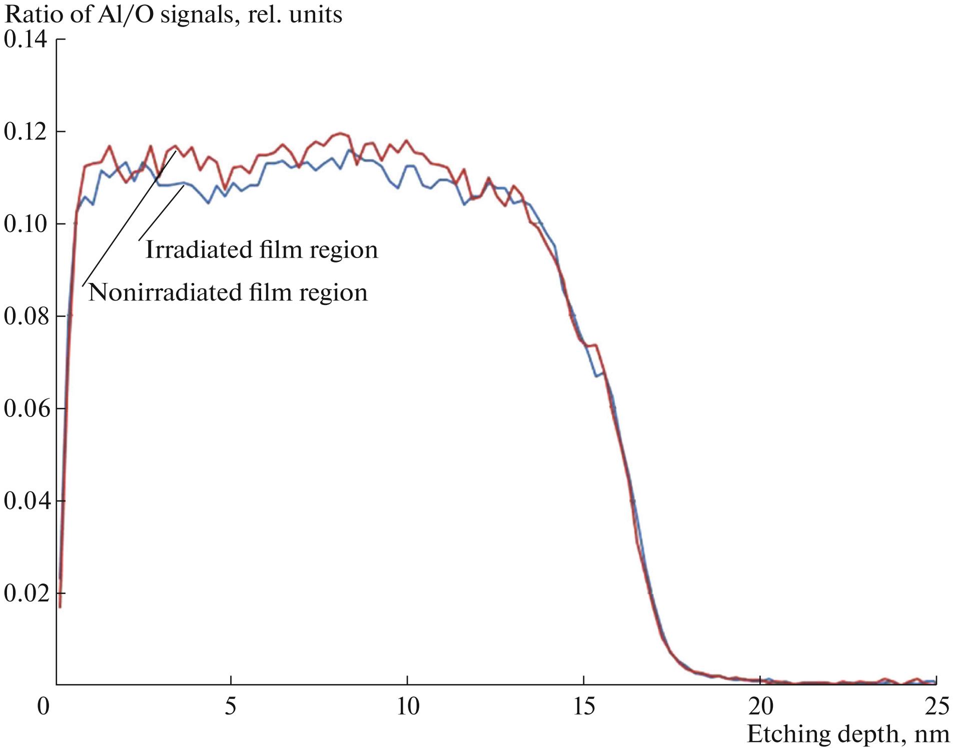

**Fig. 4.** (Color online) Depth distributions of the aluminum-to-oxygen (Al/O) ratio determined by SIMS analysis in the irradiated and nonirradiated regions of the alumina film on substrate *L4*.

It follows from the data that the depth distributions of the elemental aluminum-to-oxygen ratio at the irradiated and nonirradiated regions of $Al_2O_3$ films on substrate *L4* match within the experimental error.

## CONCLUSIONS

It was found that laser radiation with a wavelength of 970 nm and a power density of 0.29–2.10 W/cm$^2$ applied at the stages of reactor purging to the surface of silicon substrates in the process of ALD of alumina films from TMA and water vapor

(i) does not alter the rate of deposition of alumina films;

(ii) does not alter the surface relief (roughness) of alumina films;

(iii) does not alter the depth profile of the chemical composition of alumina films;

(iv) reduces the average density of irradiated regions of alumina films by 5–10% relative to the density of nonirradiated regions.

Our assumption that the interatomic distances in the deposited alumina films increase under laser irradiation needs to be verified by the results of additional extended studies. XAFS spectroscopy may be used in these extended studies, since the processing of XAFS spectra provides data on the interatomic distances. However, it is an indirect method based on calculations, while a high-resolution electron microscope allows one to directly measure the interatomic distance in electronic images of the cross section of irradiated and nonirradiated regions of an $Al_2O_3$ film.

It should be noted that the studied process of ALD of alumina films is exactly opposite in nature to the process of CVD of $Al_2O_3$ films with continuous reagent (precursor) supply. In the latter processes, photon and laser irradiation considerably enhance the rates of deposition of alumina from gas reagents onto the surface of silicon slices and strongly affect the chemical composition and the surface relief of deposited films [1].

Therefore, the experimental verification of the fact that the ALD mechanism is, unlike CVD, only marginally affected by laser irradiation is scientifically important and opens up new avenues for research. This research should clarify why discrete chemical processes are more resistant to external effects than continuous processes.

## ACKNOWLEDGMENTS

The structure and the composition of films were studied at the common use center "Microsystems Technology and Electronic Component Base" of the National Research University of Electronic Technology supported by the Ministry of Education and Science of Russia (contract no. 14.594.21.0012, unique identifier RFMEFI59417X0012).

## REFERENCES

1. V. Yu. Kireev and A. A. Stolyarov, *Microelectronics Technology. Chemical Vapor Deposition* (Tekhnosfera, Moscow, 2006) [in Russian].
2. M. Gutsche, H. Seidl, T. Hecht, and U. Schroeder, "Atomic layer deposition for advanced DRAM applications," in *Future Fab,* No. 14 (Technology Publ., London, UK, 2003), pp. 213–217.
3. T. V. Semikina, V. N. Komashchenko, and L. N. Shmyreva, "Nanotechnology: the basics of the method of atomic layer deposition, equipment, application in nanoelectronics," Elektron. Svyaz', Elektron. Nanotekhnol., No. 1, 60–66 (2009).
4. *Atomic Layer Deposition for Semiconductors,* Ed. by Ch. S. Hwang and Ch. Y. Yoo (Springer Science, New York, 2014).
5. D. Vogler and P. Doe, "Atomic layer deposition special report: where's the metal?," Solid State Technol. **46**, 35–40 (2003).
6. V. B. Aleskovskii, *Stoichiometry and Synthesis of Solid Compounds* (Nauka, Leningrad, 1976) [in Russian].
7. V. B. Aleskovskii, "Structural organization of matter," Inform. List. Direkts. NII Khim. Dekanata Khim. Fak. No. 15/02(190) (2002), pp. 1–4.
8. A. A. Malygin, "Molecular layering nanotechnology (review)," Ross. Nanotekhnol. **2** (3–4), 87–100 (2007).
9. T. Suntola and J. Antson, "Surface chemistry of atomic layer deposition," US Patent No. 4058430 (1977).
10. A. P. Alekhin, G. M. Boleiko, S. A. Gudkova, A. M. Markeev, A. A. Sigarev, V. F. Toknova, A. G. Kirilenko, R. V. Lapshin, E. N. Kozlov, and D. V. Tetyukhin, "Synthesis of biocompatible surfaces by nanotechnology methods," Nanotechnol. Russ. **5**, 696 (2010).
11. A. N. Belov, E. E. Gusev, N. A. Dyuzhev, V. I. Zolotarev, and V. Yu. Kireev, "CMOS-based supercapacitor," RF Patent No. 2629364 (2016).
12. M. Putkonen and V. Tuzovskii, "New applications of atomic layer deposition," Nanoindustriya, No. 5, 18–21 (2010).
13. S. M. Repinskii, "Chemical kinetics of growth of dielectric layers," in *Modern Problems of Physical Chemistry of Semiconductor Surface* (Nauka, Novosibirsk, 1989), pp. 90–152 [in Russian].
14. E. Maiorov, "Implementation of nanotechnology atomic layer deposition on equipment of the company Beneq: from laboratory to industry," Kompon. Tekhnol., No. 10, 48–53 (2013).
15. I. M. Iskandarova, A. A. Knizhnik, E. A. Rykova, A. A. Bagatur'yants, S. Ya. Umanskii, B. V. Potapkin, and M. W. Stoker, "Film growth simulation during atomic layer deposition," Fiz.-Khim. Kinet. Gaz. Dinam., No. 4, 388–402 (2006).
16. D. S. Saiko, V. V. Ganzha, S. A. Titov, I. N. Arsent'ev, A. V. Kostyuchenko, and S. A. Soldatenko, "Water adlayers on aluminum oxide thin films," Tech. Phys. **54**, 1808 (2009).
17. B. M. Yavorskii, A. A. Detlaf, and A. K. Lebedev, *Handbook on Physics,* 8th ed. (Oniks, Moscow, 1056) [in Russian].

*Translated by D. Safin*