UDC 621.318

A. Borisova, **A. Machulyansky**, Ph.D., **M.Rodionov**, Ph.D., **V. Smilyk**, **Y. Yakimenko**, Dr.Sc.
National Technical University of Ukraine "Kyiv Polytechnic Institute",
st. Polytechnique, 16, Kiev, 03056, Ukraine.

Aluminum oxynitride dielectric films prepared by reactive sputtering

Influence of technological modes of synthesis of aluminum oxynitride films by a method of magnetron reactive sputtering on their physical and chemical parameters is probed. Studied by IR spectroscopy and Auger electron microscopy and elemental, phase and structural composition of the synthesized films. Features of spectral and electrophysical parameters of films are discussed. Chemical stability of films is probed. Recommendations about modes of synthesis of films of electrophysical parameters of films providing optimization on the given their operational properties are received. References 13, figures 3, table 1.

Keywords: aluminum oxynitride film; magnetron reactive sputtering; dielectric strength; chemical resistance; thermal stability.

Introduction

Wide use of thin-film coverings in optoelectronics, in processing systems and information storages, laser technology, and also as power effective coverings results in need of development of metal-dielectric materials with the given characteristics. One of the perspective directions of creation of such materials is formation of composition nanostructural metal-dielectric systems in which nano-sized metal switching on is distributed in a dielectric matrix [1,2].

However, support of operational stability of nano-sized metal particles is the actual task (problem) of development of nano-sized systems. In operations [1], it is shown that stability of such composite systems is defined by properties of a dielectric component (matrix). In this regard, films aluminum oxynitride, which is widely used in electronic technology thanks to its properties, are of special interest [3,4].

Analysis of modern methods of synthesis of aluminum oxynitride films gives grounds to prefer reactive magnetron sputtering, as it allows deposition at low temperature and ensure good adhesion to the substrate condensate [5-8]. To date, known for his work on development of processing techniques produce aluminum nitride films with optimized electrical and frequency characteristics [6,7]. At the same time, the structure and chemical composition of these films is not known. There is no evidence of their thermal and chemical stability, no recommendations formulated to the selection process conditions directed synthesis of aluminum oxynitride films with desired physical and chemical properties.

Aim is to study the thermo-chemical resistance, dielectric strength, optical characteristics, composition and structure of films based on aluminum oxynitride depending on the parameters of technological modes of synthesis by magnetron reactive sputtering.

Experimental technique and materials

The films were deposited on glass substrates and single-crystal silicon (plane (100) plates SBD-7,5) by reactive magnetron sputtering at a constant current in the argon/nitrogen. Variable parameters were discharge power (200-500 W), the residual gas pressure ($2\cdot10^{-3}$-$7\cdot10^{-7}$ Pa), substrate temperature (25-300 °C), while spraying (10-120 min) and bias potential on the substrate (ground substrate, a negative voltage (-50 V), high potential of 50 V).

Chemical resistance was evaluated according to the etching rate of the films and the substrate for a standard microelectronic technology etchants: concentrated nitric acid and sulfuric acid, a mixture of concentrated sulfuric acid and hydrogen peroxide in a 3:1 ratio, a mixture of 70% beam nitric acid, acetic acid and phosphoric acid in a ratio of 1:3:25 mixture of 70% aqueous potassium hydroxide solution and 3% aqueous sodium orthophosphate 8:1; concentrated mixture of ammonium fluoride and 10% hydrofluoric acid in a ratio of 3:1 [9].

Measurement of resistivity and dielectric strength (breakdown voltage) was performed according to standard procedures on structures condenser type Si — AlN — Al. The thickness and refractive index of the obtained films was calculated using a standard computer software program data from the ellipsometric measurement at a wavelength of 632,8 nm [10].

Elemental analysis for nitrogen, oxygen, aluminum films were performed using Auger electron spectroscopy [11]. The nature of the material of the films was studied by IR spectroscopy according to their differential (relative to pure silicon substrate), the transmission spectra in the 1000-400 cm^{-1} vibrations of an Al — O and Al — N [8,11].

The thermal stability of the films was studied by changing the spectra after the additional annealing at a temperature of about 1000° C for 30 min.

Results of measurements and their discussion

The synthesis conditions of the films (thickness 0,5-1,5 mm) and their composition and physical characteristics measured are shown in Table 1.

Table 1. Electrophysical properties of Aluminum Oxynitride Films

Technological parameters of a mode of evaporation of films			**Physical parameters of a film**			**Chemical parameters of a film**					
						Maintenance of elements, at. %			**Etching rate, nm/s**		
power of discharge, W	temperature of a substrate, °C	vacuum of the camera, Pa	unit resistance, Ω·m	shorting tension, V/m	refraction index	Al	N	O	acids sulfuric, nitric	mix $KOH:Na_3PO_4 = 8:1$	mix $NH_4F:HF = 3:1$
500	25	$7 \cdot 10^{-5}$	$1 \cdot 10^{9}$	$5 \cdot 10^{6}$	1,92	55	23	1	1,0	0,02	3,0
300	100	$1 \cdot 10^{-4}$	$1 \cdot 10^{10}$	$2 \cdot 10^{7}$	2,25	55	30	-	1,0	0,01	3,0
200	200	$5 \cdot 10^{-4}$	$5 \cdot 10^{8}$	$5 \cdot 10^{6}$	1,60	50	8	25	0	0,02	3,0
200	200	$7 \cdot 10^{-4}$	$7 \cdot 10^{6}$	$8 \cdot 10^{5}$	1,40	48	-	44	0	0,05	3,0

According to the detected content of aluminum, nitrogen and oxygen in the films synthesized by a formula of structure installed. At 55% alumina content and 23-30% nitrogen, which corresponds to the ratio Al:N=2:1, the film composition corresponding to the formula AlN, is confirmed that the obtained close to the atomic weight ratio of Al to the atomic weight of N — 27:14=1,92:1. With a decrease in the nitrogen content up to 8% increase in the oxygen content and up to 25% with 50% aluminum ratio of these elements (A1:O:N=6:3:1) indicates the formation of aluminum oxynitride $Al_3O_3N_4$ composition, calculated as the ratio of the atomic weights of the elements this formula (27×3:16×3:14=5.8:3.4:1) agrees well with the experimental data. Also synthesized by a film which consists predominantly of aluminum (48%) and oxygen (44%) of a 1:1 ratio with that composition can be represented by aluminum oxide Al_2O_3 ratio calculation of atomic weight — 27×2:16×3=1,12:1. Besides the basic elements (Al, O, and N) according to the Auger spectra of the compositions in the films revealed 3-10 % iron and 5-10 % silicon, which can be associated with parts of the magnetron sputtering unit and the substrate. From the table it is also clear that as the oxygen enrichment of film materials refractive index decreases from 2,25 to 1,40. Similar results were obtained for films of silicon nitride and silicon oxide [12].

Noteworthy is that the oxygen and Al_2O_3 film Al_3O_3N formed at a discharge power of 200 W and pre-evacuation of the chamber to a pressure of residual gases $7 \cdot 10^{-4}$ Pa, while the film of aluminum nitride AlN — at most 2 times the discharge power and 10 times fewer residual gas pressure. In this oxide film and aluminum oxynitride resistivity by 2-3 orders of aluminum nitride films are inferior. At the same time on chemical firmness, all three film materials differ among themselves a little.

From the data presented in Fig. 1 and 2 received a dependency of specific resistance and breakdown voltage of the temperature that the electrical characteristics are significantly improved when using RF bias on the wafers.

Thus, to obtain the Al_2O_3 film and Al_3O_3N sufficient vacuum system to evacuate residual gas pressure of about $7 \cdot 10^{-4}$ Pa, and sputtering to produce a discharge at a power of 200 W with the substrate heated to a temperature of 200° C, and for the synthesis of AlN films need to pre-evacuation pressure of at least $7 \cdot 10^{-5}$ Pa, using an RF bias potential on the substrate 50 and the discharge power of 300 W and 500 W, respectively, to substrate 100, and at a temperature of 25° C.

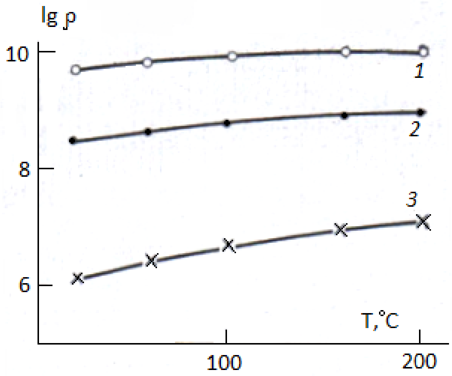

Fig. 1. Dependence of the resistivity aluminum oxynitride ρ-films on the substrate temperature: 1 − high-bias potential (50 V, 10 MHz) on the substrate 2 − constant negative potential (-50 V) on the substrate, 3 − substrate grounded

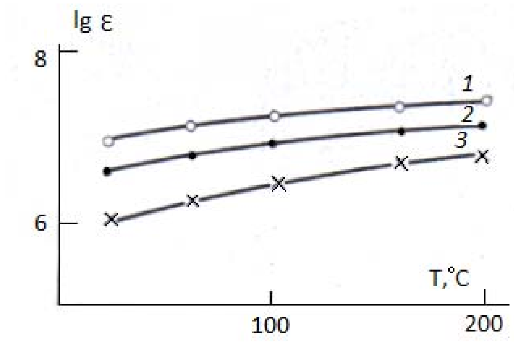

Fig. 2. Depending on the electric strength of ε-aluminum oxynitride films on the substrate temperature: *1* − high-bias potential (50 V, 10 MHz) on the substrate *2* − constant negative potential (-50 V) on the substrate, *3* − substrate grounded

Fig. 3 shows the IR transmission spectra of the films studied in the spectral range 1000-400 cm^{-1}, a typical manifestation of the oscillation frequencies of the tetrahedral [AlO_4] and octahedral [AlO_6] groups aluminosilicates, bauxite, spinel and single crystal , fine [1] and the film aluminum nitride [8, 11,12,13].

Very intense narrow band of 665 cm^{-1} range of aluminum nitride film (Fig. 1-3), according to the experimental [8] and calculated [12] data refers to fluctuations in Al — N communication coordination tetrahedron [AlN_4] which is the main structural motif AlN wurtzite lattice. Discovered the identity of the position and shape of this band in the spectra of the film and crystalline aluminum nitride is the basis to assume that the synthesized AlN films are polycrystalline with a regular orientation of the structural elements. At the same time a very broad intense absorption around 760 and 700 cm^{-1} in the spectra of oxide films (Fig. 3, 2) and oxynitride (Fig. 3, 3), respectively, aluminum may be indicative of the amorphous nature of these materials, since the presence of orientation and/or positional disorder molecular units of matter leads to a significant broadening of the spectral bands. Additional data on the nature of the synthesized film materials are received also in case of research of their thermal stability.

Thermal stability is estimated by comparing the IR spectra of the starting and annealed (1000° C, 30 min) film in a dry atmosphere and the water vapor. Identical spectra were obtained for all the annealed films (AlN, Al_3O_3N, Al_2O_3), so in Fig. 3, 4 shows a typical spectrum. New spectrum unlike raw spectra comprises two films intensive high relative to the spectra of the starting film 800 in doublets, 775 and 520, 450 cm^{-1}, which may be associated with a transition to a more ordered crystalline structure. Probably under the conditions of high temperature processing films passed their oxidation of modifications to the single-crystal aluminum oxide. This assumption is supported by the similarity of MK-detected spectra (Fig. 3, *4*, 5) and annealed films corundum.

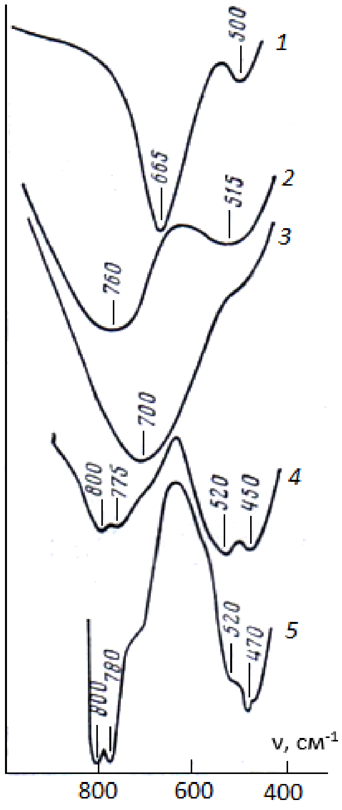

Fig. 3. Infrared transmission spectra of films: *1* − AlN, *2* − Al_2O_3, *3* − Al_3O_3N, *4* − AlN after annealing at 1000° C, *5* − potassium bromide tablet corundum (α-Al_2O_3)

Thus, with the help of IR spectra shows that the aluminum nitride AlN films are polycrystalline and are identified by a narrow intense band about 665 cm^{-1}, and the oxide film Al_2O_3 and aluminum oxynitride Al_3O_3N form a disordered structure and characterized by IR spectra in a broad intense band respectively at 760 and 700 cm^{-1}.

Conclusions

The method of magnetron reactive direct current sputtering by a variation of technological modes of synthesis created films of different composition: AlN aluminum nitride, Al_3O_3N aluminum oxynitride and Al_2O_3 aluminum oxide.

The assessment of the received films on unit resistance, breakdown strength, and coefficient of refraction, chemical stability and thermal stability is carried out.

It is shown (TABLE I) that the maintenance of the phase AlN in films can be raised in a directional way by change of technological parameters a ratio of reactive gases, capacities of discharge, temperature of a substrate and bias voltage given on it.

Synthetizing of a film can beat are recommended for use in electronics as browning and insulation layers and to formation on their basis of composition coverings with the given optical characteristics.

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Поступила в редакцию 21 мая 2015 г.

УДК 621.318

О.В. Борисова, **О.В. Мачулянський**, канд. техн. наук, **М.К. Родіонов**, канд. фіз.-мат. наук,
В. Смілик, **Ю.І. Якименко**, д.-р. техн. наук
Національний технічний університет України "Київський політехнічний інститут",
вул. Політехнічна, 16, корпус 12, Київ, 03056, Україна.

Діелектричні плівки оксинітриду алюмінію отримані реактивним розпиленням

Вивчено вплив на електрофізичні та хімічні властивочті діелектричних плівок оксинітриду алюмінію технологічних режимів їхнього формування методом реактивного магнетронного напилення. Досліджено методом ІЧ-спектроскопії, ОЖЕ-спектроскопії та електронної мікроскопії електронний та структурний склад синтезованих плівок. Обговорено властивості спектральних та електрофізичних параметрів (питомого опору, електричної міцності, термічної стабільності та хімічної стійкості) плівок. Надано рекомендації щодо режимів синтезу плівок з метою забезпечення оптимізації електрофізичних параметрів на задані експлуатаційні властивості. Бібл. 13, рис. 3, табл. 1.

Ключові слова: *плівки оксинітриду алюмінію; магнетроне реактивне розпилення; електрична міцність; хімічна стійкість; термічна стабільність.*

УДК 621.318

А.В. Борисова, **А.В. Мачулянский**, канд. техн. наук, **М.К. Родионов**, канд. физ.-мат. наук,
В. Смилык, **Ю.И. Якименко**, д-р. техн. наук
Национальный технический университет Украины «Киевский политехнический институт»,
ул. Политехническая, 16, корпус 12, г. Киев, 03056, Украина.

Диэлектрические пленки оксинитрида алюминия полученные реактивным распылением

Изучено влияние на электрофизические и химические свойства диэлектрических пленок оксинитрида алюминия технологических режимов их формирования методом реактивного магнетронного распыления. Исследован методом ИК – спектроскопии, ОЖЕ – спектроскопии и электронной микроскопии элементный и структурный состав синтезированных пленок. Обсуждены особенности спектральных и электрофизических параметров (удельного сопротивления, электрической прочности, термической стабильности и химической устойчивости) пленок. Даны рекомендации режимов синтеза пленок, обеспечивающих оптимизацию электрофизических параметров пленок на заданные эксплуатационные свойства. Библ. 13, рис. 3, табл. 1.

Ключевые слова: *пленки оксинитрида алюминия; магнетронное реактивное распыление; электрическая прочность; химическая устойчивость; термическая стабильность*.

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