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> PHYSICAL CHEMISTRY OF NANOCLUSTERS AND NANOMATERIALS

Surface Nanostructures Based on Tantalum and Aluminum Oxides

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Abstract—Generalized results from investigations into the processes of formation of tantalum and aluminum oxide nanostructures and their multilayered systems produced by the method of molecular lamination on a (100) silicon surface and aluminum are reported. Conditions for the layer-by-layer growth of oxide structures and multilayered low-dimensional systems with alternating zones of the said oxides are determined. Dielectric characteristics of the synthesized nanostructures are evaluated.

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INTRODUCTION

Progress in the chemical nanotechnology of submicron-scale structures involving surface chemical reactions that form the basis of the atomic layer deposition (ALD technology), better known in Russia as the molecular lamination (ML) method [1-3], requires the solving of a number of problems related to establishing the properties of nanostructures and regular features of their formation. One major problem is determining the conditions for the mechanism of their layer-by-layer synthesis, excluding the stage of threedimensional nuclei formation and ensuring the matrix synthesis of low-dimensional structures with the possibility of verifying composition and thickness at the monolayer level. It should be noted that chemical methods for the synthesis of low-dimensional objects are an integral part of a vigorously progressing chemical nanotechnology for the production of new materials having different end uses, and of nanoelectronic systems in particular. Employing the gas-phase feed of reagents and being self-organizing in character, such processes allow entire batches of goods to be treated at once, making them more profitable.

Successful application of ALD technology in tackling certain problems in electronics has been reported in publications abroad, e.g., [4–6].

Submicron layers of aluminum and tantalum oxides are of practical significance as they have high dielectric characteristics. Multilayered nanostructures based on these materials ought to possess special properties such as dielectric superlattices, the characteristics of which would depend on the composition, the sequence of layers, and the distribution of potential.

This paper describes the generalized results of investigations into synthesis processes and the basic dielectric characteristics of nanolayers of tantalum and aluminum oxides and multilayered systems of them deposited by the ML method on a silicon surface and aluminum films on silicon.

EXPERIMENTAL

The nanolayers were synthesized on freshly etched silicon (KEF-7.5, (100) orientation) and vacuum-sputtered aluminum films on silicon ~0.2 μ m thick. The process was implemented in a vacuum flow-through installation (with residual gas pressure of no more than 10⁻¹ Pa), ensuring interaction between the metal chloride vapor and surface hydroxyl groups and subsequent hydrolysis with water vapor for recovery of the hydroxyl coating.

The reactions for the silicon matrix can be written in the form

$$(\equiv \text{Si}-\text{OH})_m + \text{MCl}_n$$
(I)

$$\rightarrow (\equiv \text{Si}-\text{O}-)_m \text{MCl}_{n-m} + m \text{HCl},$$

$$(\equiv \text{Si}-\text{O}-)_m \text{MCl}_{n-m} + (n-m)\text{H}_2\text{O}$$
(II)
$$\longrightarrow (\equiv \text{Si}-\text{O}-)_m \text{M}(\text{OH})_{n-m} + (n-m)\text{HCl}.$$

Repeated reactions (I) and (II) and the intermediate removal of excess reagents and reaction products led to formation of an oxide layer of the required thickness (d), which was proportional, as was found in [2, 3], to the number of the treatment cycles (N):

$$d = d_0 N, \tag{1}$$

where d_0 is the proportionality factor characterizing the structure of the synthesized layer and indicating average thickness of the film in a single cycle of treatment with one component or another.

A comparison of d_0 , now called "the layer growth parameter," and the metal—oxygen interlayer spacing in the oxide structure allows us to assess the level of

surface filling and is one criterion for determining the layer formation mechanism. Of greatest interest is a lamination mechanism that can operate under the nonequilibrium conditions of reactions (I) and (II) upon the limiting hydroxylation of the surface and sufficient activity of the OH groups. However, hydroxyl groups of monocrystalline silicon with an oxide <3 nm thick exhibit weak proton-donor properties in surface reactions [7].

The same is true of the aluminum matrix surface. Although the hydroxyl groups in the surface layer of the aluminum oxide have a sufficiently high protondonor capacity [8], the electron-saturated core of the metal matrix suppresses the inductive effect that facilitates protonization of the hydroxyl groups. We therefore proposed using triethylamine (TEA) [9] to activate surface reactions. Possessing high proton-acceptor properties, this reagent can perform a number of functions simultaneously: it can stabilize hydroxyl coating with additional hydrogen bonds, activate a reaction by forming an intermediate complex, and bind liberated hydrogen chloride, thereby ensuring completeness of the reactions. In synthesizing triethylamine, which is not inclined toward nucleophilic substitution reactions, we can add water vapor and $(H_2O + N(C_2H_5)_3)$ simultaneously, and the complex formed on the surface (e.g., \equiv Si-OH---N(C₂H₅)₃) facilitates protonization of the hydroxyl groups.

Since the topology of a hydroxyl coating on silicon with a thin oxide layer at $T_s > 450$ K is capable of ensuring the chemical bonds of a halogenide with not more than two hydroxyl groups [7], the chemisorption of a halogenide (e.g., TaCl₅ with TEA) can be visualized in the form



This scheme depicts only the stoichiometry of the surface reaction rather than the coordination of the metal in the oxide being formed.

The thickness of the synthesized nanolayers was determined from ellipsometric measurements of polarization parameters Δ and Ψ ; it was also calculated as an approximation of the Drude–Tronston onelayer model [10]. The parameters Δ and Ψ were measured on an ellipsometer in the PQSA [11] arrangement with a fixed compensator. The source of linearly polarized light was an LG-75 laser with an emission wavelength of 632.8 nm. To improve measurement accuracy, the light beam was in some cases (the initial stages of growth) subjected to magnetic modulation, and parameters Δ and Ψ were measured to within $\pm 0.01'$.

Composition of the ultrathin layers was monitored according to the XPS data, using NP-5950A (Al K_{α} radiation, $E_{K_{\alpha}} = 1486 \text{ eV}$) and SER-1 (Mg K_{α} radiation, $E_{K_{\alpha}} = 1253 \text{ eV}$) spectrometers. The energy was measured against the C1 $s_{1/2}$ carbon standard with $E_{\text{st}} = 285.0 \text{ eV}$. At these energies, the probe penetrated the surface layer to a maximum depth of 8 nm [12]. The energy lines of the elements under study (E_s) were identified using data from [13, 14], while layer composition was determined from the relationship [12]

$$I_1/I_2 = n_1 \sigma_1 \sqrt{E_{K_2}} / n_2 \sigma_2 \sqrt{E_{K_1}},$$
 (2)

where I_1 and I_2 are the intensities of the examined lines of the atoms under study; σ_1 and σ_2 are the relative cross-sections of ionization for the studied levels; n_1 and n_2 are the concentrations of the studied atoms; and E_{K_1} and E_{K_2} are the kinetic energies of knockedon electrons ($E_K = E_{K_{\alpha}} - E_s - F_s$, where F_s is the electron work function of the spectrometer material). Spectra were computer-processed using a special program with Gaussian approximation of the curves. Layer composition was also identified from ellipsometric observation of the refraction index determined by the Holmes method [11].

Kinetic characteristics of the metal halogenide and water were subjected to ellipsometric analysis so as to establish conditions for the limiting filling of the surface with groups synthesized by reactions (I) and (II) at a given synthesis temperature and vapor pressure. The evaluation criterion was the dependence of the growth parameter (the thickness of the formed oxide, reduced to one treatment cycle) on the time of contact between the reagent and the substrate. An analysis of this dependence at different temperatures of the substrate and different pressures of the halogenide showed (Fig. 1) that within the range of the studied reagent vapor pressures, the surface filling kinetics depended essentially on the substrate temperature only.

Halogenide chemisorption was of a similar character for both oxides (Fig. 1). At $T_s < 423$ K and a halogenide vapor pressure p = 0.5-10 Pa, parameter d_0 increased continuously, pointing to polymolecular adsorption of the halogenide. When the substrate temperature was higher, the surface was saturated with oxide groups (Fig. 1). This suggested the process was of a self-limiting nature. Considering these data, the time of contact between vapors of halogenide and water at $p \approx 1.3$ Pa and ~10 Pa, respectively, was chosen to be 30 s for AlCl₃ and 60 s for TaCl₅. These times were used in all our subsequent experiments.

Analysis of the growth dynamics of the Al_2O_3 and Ta_2O_5 layers (Fig. 2) demonstrated that at $T_s = const$,



Fig. 1. Kinetics of surface filling with components during formation of Al_2O_3 (*1–3*) and Ta_2O_5 (*1'–3'*) at substrate temperatures $T_s = 403$ (*1, 1'*), 523 (*2, 2'*), and 603 K (*3, 3'*); p = 1.3 Pa.

the dependences d = f(N) followed Eq. (1) over the studied range of N. This indicated the surface reactions were of a sustained nature, and that equal amounts of product were formed in each reaction cycle. In the case of aluminum oxide, (Fig. 2, 1) the value of d_0 was in better agreement with the calculated data if the surface reactions were assumed to involve the Al₂Cl₆ dimer dominant in the composition of the halogenide vapor and having an orientation that led to the formation of two aluminum-oxygen layers:



Scheme (IV) does not show the formation, analogous to reaction (III), of an intermediate complex with thriethylamine; neither is the actual coordination of aluminum in the forming oxide layer reflected.

Analysis of the series of dependences d = f(N), obtained for the Al₂O₃ and Ta₂O₅ layers at different temperatures of the substrate, allowed us to establish how this factor influenced the layer growth parameter (Fig. 3). The mechanism of layer formation and the conditions for layer-by-layer growth can be inferred from the dependence $d_0 = f(T_s)$. The large values of d_0 at low temperatures and the reduction in this parameter with rising T_s suggested polymolecular sorption of the reagents at $T_s < 450$ K and their interaction in the adsorbed layer, followed by the formation of hydrated oxide. At T > 450 K, the value of d_0 approached the double metal-oxide interlayer spacing for the given oxide. These conditions could therefore be characterized as the layer growth conditions. For comparison, Fig. 3 (1' and 2') depicts $d_0 = f(T_s)$ for Ta₂O₅ and Al₂O₃ layers synthesized in the absence of TEA. In this case, halogenide chemisorption was of an expressed activation character at $T_s > 453$ K and layer growth could be effected only at $T_s > 550$ K.

The use of TEA in the synthesis process eliminated the activation barrier, extending the temperature range of layer growth almost by 100 K, into the low-temperature region (Fig. 3). At higher synthesis temperatures, the decline in d_0 was due to partial dehydroxylation of



Fig. 2. Growth dynamics of Al_2O_3 (*1*) and Ta_2O_5 (*2*) films on a silicon matrix at $T_s = 523$ K with TEA.

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Fig. 3. Effect of synthesis temperature on the growth parameter of Al_2O_3 (*1*, *1*) and Ta_2O_5 (*2*, *2*) layers on silicon with (*1*, *2*) and without (*1'*, *2'*) exchange activator (triethylamine).

the surface and the formation of two-dimensional island structures.

Composition of the synthesized products was studied by the methods of IR and XPS spectroscopy for films more than 10 nm thick. According to the XPS data, the lines characteristic of halogenides (2*s*-, and 2*p* levels) were absent at energies of 75–120 eV, while

lines typical of 1*s* levels of nitrogen of the NR₄⁺ group were absent near energies of 401–402 eV [12]. TEA was then fully desorbed during the synthesis process. Peaks with energies of 100–150 eV, which are characteristic of 2*s* and 2*p* levels of silicon, were not detected for either Ta₂O₅ or Al₂O₃ layers with d > 5 nm, indicating layer continuity at this thickness.

The oxygen-metal ratio in the oxide layer at different synthesis temperatures was found from the area of the peaks of oxygen ($E_b = 530-534 \text{ eV}$) and the respective metals ($E_b = 74.6 \text{ eV}$ for Al_{2p} , $E_b = 118.8 \text{ eV}$ for Al_{2s} , and $E_b = 26.8 \text{ eV}$ for Ta_{4f}). The relevant results

 Table 1. Oxygen-metal ratio in aluminum and tantalum oxide layers at different synthesis temperatures

<i>T</i> _s , K	[O]/[Al]	[O]/[Ta]
423	4.0	4.6
473	2.3	3.0
523	1.8	2.6
553	1.5	2.5
573	1.6	2.5
773*	1.5	2.5

are given in Table 1. This table also presents data (marked with asterisks) for layers that were subjected to thermal treatment in a vacuum (10^{-2} Pa) at T = 773 K for 1 h. According to these data, the oxide nanostructures remained virtually unhydrated at $T_s > 523$ K and their composition corresponded to Ta₂O₅ and Al₂O₃, respectively. The high oxygen concentration was most probably due to hydration of the oxides at low synthesis temperatures and the small contribution from the oxygen of the matrix oxide layer at high synthesis temperatures (mainly Al₂O₃).

IR spectroscopic analysis by the method of multiple disturbed total internal reflection (MDTIR) of aluminum and tantalum oxide layers synthesized on silicon elements at $T_s = 553$ K confirmed the XPS data. One could, for example, clearly see the absorption bands characteristic of Si–O–Al bonds in aluminum silicates with v = 1130 cm⁻¹ and those with v = 744 and 835 cm⁻¹, typical of Al-O bonds with six- and four-coordination aluminum [15].

Electron diffraction analysis of the structure of synthesized oxide films more than 10 nm thick showed that Ta₂O₅ layers were amorphous over the temperature interval. Films of Al₂O₃ deposited at $T_s < 450$ K were amorphous too, while α -Al₂O₃ was observed in them at high temperatures.

The similar tension for vapors of the tantalum and aluminum halogenides, along with the similar temperature conditions for layer-by-layer growth of their oxide systems (Fig. 3), considerably simplified synthesis of multilayered structures on their basis, obviating the need to heat the entire system of halogenide vapor feed to the reactor to the temperature of the halogenide source.

Since synthesis of aluminum oxide layers by treatment of the surface of the tantalum oxide layer with aluminum halogenide vapor might involve the substitution reaction

$$\operatorname{Ta}_2 \operatorname{O}_5 + \operatorname{AlX}_3 \longrightarrow \operatorname{Al}_2 \operatorname{O}_3 + \operatorname{TaX}_5, \qquad (V)$$

the thermal effects were estimated and the equilibrium constant $(K_{f,T})$ was calculated by the Temkin–Schwarmann method, using equations for the isobaric potential $\Delta G_T = 2.3RT\log K_{f,T}$ and $\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$.

Calculations performed for AlCl₃ and AlBr₃ demonstrated (Table 2) that the substitution reaction can be eliminated at $T_s < 470$ K for AlBr₃ and at $T_s < 600$ K for AlCl₃. With this in mind, multilayered systems were synthesized using tantalum and aluminum chlorides at $T_s = 473$ K. This corresponded to the conditions of layer-by-layer growth for each component (Fig. 3).

Ellipsometric analysis of the growth dynamics of multilayered nanostructures [16] revealed that linear dependence d = f(N) with a parameter d_0 characteristic of the oxide (≈ 0.3 nm for Ta₂O₅ and 0.45 nm for Al₂O₃) (Fig. 2) persisted within layers of each oxide,

suggesting that the mechanism of their layer-by-layer formation was maintained.

The composition and the distribution profile of elements were studied according to synthesized structure by the methods of XPS and Auger spectroscopy, taking two-layer $Si-Al_2O_3-Ta_2O_5$ and $Si-Ta_2O_5-Al_2O_3$ systems with layers up to 20 nm thick each. The XPS spectra did not exhibit the energy maxima characteristic of chlorine and silicon, testifying to the completeness of surface reactions and the continuity of the deposited layers at the said thickness.

Lines with $E_b = 118.9$ and 74.8 eV (corresponding to 2s and 2p levels of Al) and a line with $E_b = 26.8$ eV (typical of 4f levels of Ta) were clearly identified in the XPS spectra.

Examination of the Auger spectra from layer-bylayer etching with argon ions (etching rate ~0.5 nm/min) showed that the distribution of Ta and Al in the nanostructured systems with d > 10 nm corresponded to alternation of their oxide layers during synthesis (Fig. 4). It should be noted that, in the case of multilayered nanostructures synthesized with aluminum bromide at $T_s = 573$ K, there was no clearly defined zonal distribution of Ta and Al but rather a mixture of oxides. This confirmed the validity of assessing synthesis conditions from changes in the isobaric potential of the system. A signal from the silicon matrix appeared only after a 40-min etching period; at the given etching rate, this was in good agreement with the total thickness of the oxide nanostructure.

Electrophysical parameters were measured on nanostructures ~60 nm thick synthesized on aluminum films. These nanostructures were synthesized with TEA and were formed according to analogous laws. The effect of high-temperature (T = 873 K) thermal treatment was studied, taking structures with a silicon matrix as samples. Vacuum-evaporated nickel films served as electrodes.

Zonal distribution of the metal in the oxide nanostructure (Fig. 4) ought to result in the properties of the nanostructure differing from those of the oxide mixture. The most characteristic parameter is the permittivity (ϵ). This was determined by measuring the capacitance of the system on samples having a total thickness of nearly 60 nm. Both the thickness of each layer d_i (Al₂O₃) and d_i (Ta₂O₅) and their alternation were different in the test samples. A comparison of experimental values of the permittivity of multilayered systems with values calculated in terms of the Landau-Lifshitz model for a statistical mixture of dielectrics [17] showed a considerable difference in all the cases (Table 3). Only when the samples were heat treated for two hours (T = 873 K) did values of ε approach those calculated for a mixture of dielectrics, with the best match observed in samples with a thin layer (d_i , $d_i \cong 5$ nm) of at least one of the system components (Table 3, Nos. 1, 3, and 7). This suggested a zonal distribution of the oxides in the dielectric and a



Fig. 4. Intensities of Auger peaks of (1) oxygen, (2) aluminum, (3) tantalum, and (4) silicon during layer-by-layer etching of $Si-Ta_2O_5-Al_2O_3$ (a) and $Si-Al_2O_3-Ta_2O_5$ (b) nanostructures.

noteworthy contribution from the diffusion processes (T = 873 K) only at d < 5 nm.

The conductivity (σ , Ω^{-1} cm⁻¹) of the multilayered nanostructures changed from 10^{-12} in Ta₂O₅ to 10^{-14} in Al₂O₃ [16]. At d_i , $d_j > 5$ nm it was described well by the relationship for an equivalent circuit if the multilay-

Table 2. Calculated ΔG_T° (kJ/mol) and $K_{f,T}$ for reaction (5)

T _s , K	ΔG°		K _{f,T}		
	AlBr ₃	AlCl ₃	AlBr ₃	AlCl ₃	
400	10.01	18.2	-1.35	-2.38	
420	4.55	16.41	-0.39	-2.04	
450	0.70	13.73	-0.81	-1.60	
470	-3.26	11.94	0.36	-1.32	
500	-4.60	9.25	0.48	-0.95	
550	-6.32	4.77	0.60	-0.45	
600	-10.51	-0.3	0.92	2.61	

No.	<i>d_i</i> , nm	d_j , nm	Alternation of oxide layers	ε ₁	ε2	ε ₃
1	5	5	atatatatat	13.6	14.8	14.8
2	25	25	at	13.7	14.8	14.1
3	10	5	tatatat	12.2	13.0	12.8
4	20	10	tata	12.2	13.0	12.7
5	10	20	atat	15.8	16.9	16.2
6	10	50	at	18.1	19.35	18.5
7	5	20	atata	17.7	18.7	18.7

Table 3. Permittivity (ϵ) of multilayered Al₂O₃-Ta₂O₅ nanostructures of different compositions

Note: $d_i = Al_2O_3$ layer thickness; $d_j = Ta_2O_5$ layer thickness; a, t = alternation of oxide layers, a = aluminum oxide layer, t = tantalum oxide layer; ε_1 , ε_2 , and ε_3 = experimental, calculated, and experimental (following thermal treatment) values.

ered structure was viewed as a chain of series-connected resistors with the conductivities σ_i and σ_i :

$$1/\sigma = \sum (1/\sigma_i) + \sum (1/\sigma_j).$$
(3)

The relationship (3) was not fulfilled if at least one component of the structure was <5 nm thick. This was most likely due to manifestation of the charge transfer tunneling mechanism, and to conditions at the interfaces of the multilayered structure.

CONCLUSIONS

On the whole, the regular features established for formation of nanostructures of Ta₂O₅ and Al₂O₃ oxides and their multilayered systems reflect a general tendency that the temperature factor influences the growth mechanism of ML-deposited layers. It was shown in particular that formation of Al_2O_3 and Ta_2O_5 layers by alternate chemisorption of vapors of metal halogenide and water can be accomplished in three ways: reaction between components in a polymolecular adsorbed layer and the formation of hydrated oxides; successive buildup of monomolecular layers (layer-by-layer growth); and formation and further development of two-dimensional island structures. The use of TEA as the exchange activator in the synthesis process intensifies halogenide chemisorption, stabilizes the process of oxide layer formation, and extends the temperature range of layer-by-layer growth. Evaluation of basic dielectric characteristics of the synthesized nanostructures showed that their parameters allow use of the molecular lamination method for the synthesis of dielectric structures (including multilayered structures) in submicron elements of micro- and nanoscale electronic systems.

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