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Growth and Properties of Al_2O_3 and SiO_2 Nanolayers on III–V Semiconductors

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Abstract—We describe atomic layer deposition of silica and alumina layers on GaAs, InAs, and InSb substrates. The conditions for layer-by-layer growth of surface nanostructures are established, and some of their dielectric parameters are evaluated.

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INTRODUCTION

Advances in the fabrication of various nanodevices depend crucially on the development of processes for the synthesis of appropriate materials and knowledge of the fundamental mechanisms underlying the behavior of nanosystems [1]. In particular, intensive effort has been concentrated on novel electronic technologies for the atomic-scale fabrication of solid-state nanostructures.

The advent of molecular beam epitaxy [2] has considerably extended the possibilities of vacuum technology and has made it possible to overcome a number of challenges in microprocessor engineering. At the same time, though offering a number of indisputable advantages, molecular beam epitaxy requires very costly equipment, which has stimulated the search for alternative approaches.

In recent years, atomic layer deposition (ALD) has been the subject of intense attention as a process for growing high-quality ultrathin layers [3–5]. The advantages of this technology and its potential for fabricating submicron-sized components of integrated devices have been demonstrated in several studies [6–8]. ALD takes advantage of surface chemical processes previously referred to as molecular layering, whose physicochemical foundations were developed as early as the 1970s [9]. Chemical processes for the synthesis of low-dimensional systems are an integral part of the rapidly growing chemical nanotechnology of novel materials for a variety of specialty applications, particularly for nanoelectronic systems. Such processes, which utilize vapor phase delivery of reactants and take advantage of self-organization, are readily amenable to large-scale processing and, therefore, commercially viable.

In this paper, we report the growth of silica and alumina nanolayers by ALD on GaAs, InAs, and InSb substrates and the main dielectric properties (electrical conductivity and dielectric permittivity) of the nanolayers.

EXPERIMENTAL

The use of surface chemical reactions, basic to the ALD process, allows one to grow low-dimensional structures with their composition and thickness controlled on a monolayer scale. In this approach, the growth of oxide layers involves, as a key step, self-limiting chemisorption of a metal halide (MCl_n) and water vapor under limiting surface coverage conditions. For example, the process on hydroxylated surfaces (symbol |) can be run according to the schemes

$$|\!-\!\mathrm{OH})_m + \mathrm{MCl}_n \longrightarrow |\!-\!\mathrm{O}\!-\!)_m\,\mathrm{MCl}_{n-m} + m\mathrm{HCl}, \quad (1)$$

$$\begin{gathered} |\!-\!\mathrm{O}\!-\!)_m\mathrm{MCl}_{n-m} + (n-m)\mathrm{H_2O} \longrightarrow \\ \longrightarrow |\!-\!\mathrm{O}\!-\!)_m\mathrm{M(OH)}_{n-m} + (n-m)\mathrm{HCl}. \end{gathered} \quad (2)$$

The value of m depends on the surface density of hydroxyls; e.g., $m \simeq 2$ for silicon surfaces [10]. Repeating reactions (1) and (2) many times and intermittently removing the reaction products and excess reactants, one can grow an oxide layer of predetermined thickness. In such processes, two important conditions must be met.

First, the growth temperature of AB film, T_s, must meet the relation

$$T^{\bullet}_{\mathrm{A}}, T^{\bullet}_{\mathrm{B}} \le T_{\mathrm{s}} \le T^{\bullet}_{\mathrm{AB}}, \quad (\mathrm{I})$$

where $T^{\bullet}_{\mathrm{A}}$, $T^{\bullet}_{\mathrm{B}}$, and $T^{\bullet}_{\mathrm{AB}}$ are the critical condensation temperatures of components A and B and compound AB, respectively. This condition rules out direct condensation of component A or B, so that the process is limited to the formation of a chemisorbed layer.

Second, the surface reactions (1) and (2) should take place under nonequilibrium conditions in order to reach completion. To this end, surface hydroxyls must exhibit sufficiently high reactivity. Evaluation of

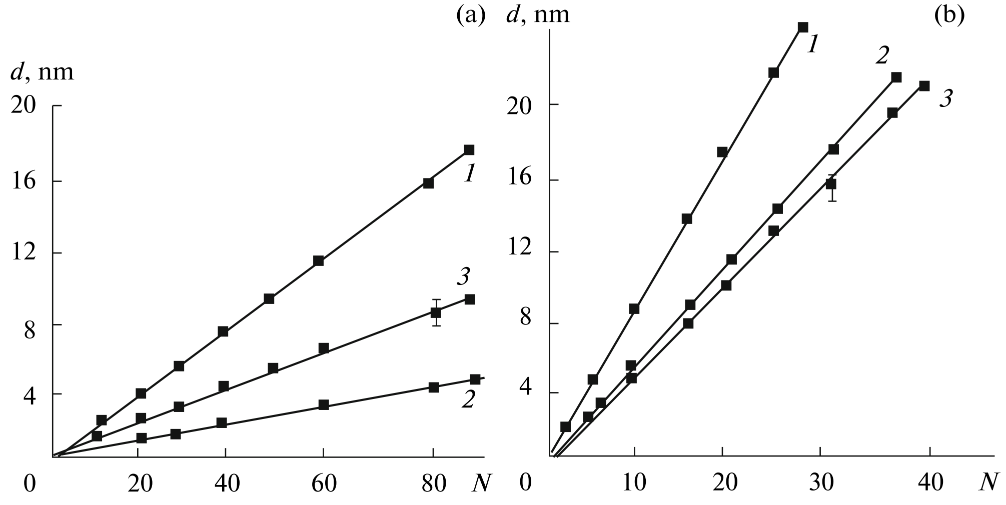


Fig. 1. Layer thickness vs. number of deposition cycles for (a) SiO_2 and (b) Al_2O_3 layers grown on (100) GaAs at a vapor pressure of 1.3 Pa and T = (*1*) 403, (*2*) 453, and (*3*) 523 K.

their reactivity on gallium arsenide using the Taft inductive constants gives $\sigma_I = 5.1$ [11]. This value slightly exceeds that for silica, on which such reactions occur rather readily [9]. It is, therefore, reasonable to expect that hydroxyls on such surfaces will exhibit sufficient reactivity with silicon chloride and aluminum chloride vapors ($\sigma^*_{\mathrm{Cl}} = 2.88$). To raise the reaction yield in step (2), triethylamine can be used as an exchange activator, which is introduced together with water vapor. In addition, this approach makes it possible to stabilize the hydroxyl layer and to reduce the layer-by-layer growth temperature [12, 13].

The substrates used were gallium arsenide ((100)-orientated AGChT-23-17 and (110)-oriented AGE-4-16), indium arsenide ((111) and (100) IMN10/PAI-380-25.5 epitaxial structures), and indium antimonide ((111)-oriented ISE-0) wafers, which were precleaned by etching in a methanolic solution of bromine (1–5% Br). According to ellipsometric data, the thickness of the residual oxide layer on all of the substrates was within 2 nm.

Oxide nanolayers were grown using reactions (1) and (2), by sequentially exposing the surface of the substrates to appropriate metal chloride (p = 1–10 Pa) and water ($p \simeq$ 100 Pa) vapors and intermittently removing the reaction products and excess reactants. The process was run in a flow reactor evacuated to a residual pressure no higher than 0.1 Pa.

The thickness of the deposited layers was evaluated from the ellipsometric parameters Δ and Ψ in the Drude–Tronston one-layer model [14]. Δ and Ψ were measured using a fixed-compensator ellipsometer in the PQSA arrangement [15]. As a linearly polarized light source, we used a 632.8-nm LG-75 laser beam, which was magnetically modulated to improve the measurement accuracy. The uncertainty in the ellipsometric parameters was within ±0.01'. Ellipsometric determination of the refractive index of the grown structures was used to assess their composition, which was also determined by X-ray photoelectron spectroscopy (XPS) on HP-5950A (AlK_α X-ray source, EK_α= 1486 eV) and SER-1 (MgK_α X-ray source, EK_α = 1253 eV) spectrometers.

The dielectric parameters of the layers were determined on both the substrates and ~0.1-μm-thick aluminum films grown on silicon by vacuum evaporation.

The electrical properties of the oxide layers were studied using EM-1 and IT-12 electrometers.

RESULTS AND DISCUSSION

Our results on the growth kinetics of the oxides under consideration at various substrate temperatures (Fig. 1) and reactant vapor pressures indicate that the thickness of SiO_2 and Al_2O_3 layers, d, is a linear function of the number of deposition cycles, N. This indicates that the hydroxides involved retain their reactivity and that the same amount of the synthesized compound is deposited in each cycle. The effect of substrate orientation was insignificant. In all instances, the layer thickness was proportional to the number of surface processing cycles by reactions (1) and (2):

$$d = d_0 N. \qquad \text{(II)}$$

Here, the proportionality factor d_0 is the average increase in layer thickness per cycle of surface processing with one of the reactants and characterizes the structure of the deposited layer. This parameter is a key characteristic of the deposition process and allows one to determine the surface coverage and to gain insight into the mechanism of film growth.

Analysis of the $d(N)$ data obtained at various substrate temperatures allowed us to assess the effect of thermal conditions on the layer growth parameter

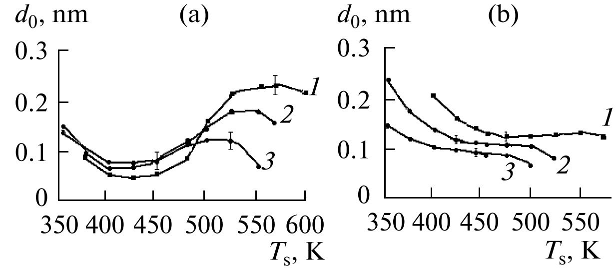
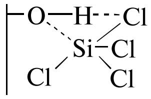


Fig. 2. Effect of substrate temperature on d_0 for (a) SiO_2 and (b) Al_2O_3 layers grown on (*1*) GaAs, (*2*) InAs, and (*3*) InSb at a vapor pressure of 1.3 Pa.

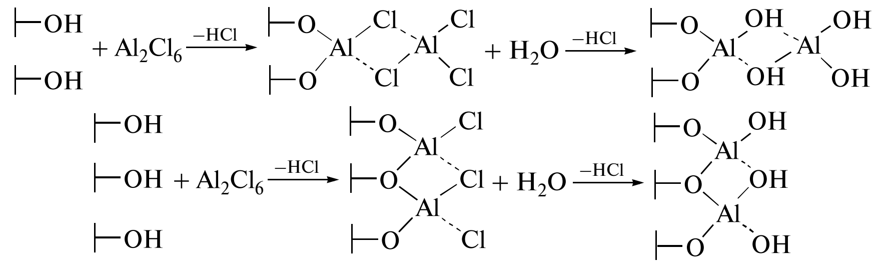
(Fig. 2), to clarify the growth mechanism of the nanostructures, and to identify the layer-by-layer growth conditions. As seen in Fig. 2, the $d_0(T_s)$ curves for SiO_2 and Al_2O_3 differ in shape and are influenced only slightly by the substrate material. This can be understood primarily in terms of the chemisorption behavior of silicon and aluminum chlorides.

The increase in surface reaction yield with increasing temperature in the case of SiO_2 layers indicates that $SiCl_4$ chemisorption is a thermally activated process. The most likely reaction is the formation of an activated complex with the hydroxyl group,



which remains stable up to ~500 K. Layer-by-layer SiO_2 growth was only achieved on GaAs and InAs at $T_s > 525$ K, when d_0 approached the silica monolayer thickness. The surface coverage of InSb with silicon–oxygen groups was within 0.5. The reduction in d_0 on InAs and InSb at $T_s > 525$ and 550 K, respectively, is due to both the reduction in the surface density of hydroxyls and the thermochemical instability of these materials in silicon halide atmospheres. The latter is supported by experimental data for GaAs: the hydroxyl groups on this material are thermally stable up to 600 K (Fig. 2).

In contrast to SiO_2, Al_2O_3 layer growth exhibited no activation behavior. The high d_0 values for alumina layers, far above the average size of aluminum–oxygen tetrahedra, are due to the fact that they grow through chemisorption of the Al_2Cl_6 dimer, which prevails in aluminum chloride vapor. Reactions (1) and (2) may then follow two major schemes (with the metal predominantly in fourfold coordination):



(3a)

(3b)

Which of these surface-reaction paths prevails depends on the topography of the hydroxyl layer. At reduced substrate temperatures ($T_s < 400$ K), where conditions (I) are not met, the density of surface hydroxyls is high, and adsorbed water molecules may be present, Al_2O_3 layers grow predominantly through reactions in the adlayer. Aluminum chloride dimers may then have various orientations, and the high d_0 values at $T_s < 400$ K point to polymolecular sorption of reactants under such conditions. Only at $T_s > 400$ K for InAs and InSb or $T_s > 475$ K for GaAs does the layer growth parameter approach twice the size of the aluminum–oxygen tetrahedra. This gives grounds to assume that, under these conditions, Al_2O_3 layers grow in layer-by-layer mode and the process is dominated by reaction (3a) with $m = 2$ (Fig. 2b).

The drop in d_0 at $T > 473$ K for InAs and at $T > 453$ K for InSb seems to be caused not so much by the reduction in the density of surface hydroxyls as by the thermochemical instability of these materials in the halide atmosphere. This is evidenced by the fact that the narrowing of the layer-by-layer growth ranges of both Al_2O_3 and SiO_2 correlates with the heats of formation of GaAs, InAs, and InSb (Fig. 2). Note that the general trends in the ALD of Al_2O_3 and SiO_2 on GaAs, InAs, and InSb are similar to those for silicon and other oxide substrates [13], indicating that these processes follow the same general mechanisms.

Structural characterization of the deposited films by electron diffraction showed that, over the entire temperature range studied, the SiO_2 layers were amorphous, independent of their thickness. The Al_2O_3 layers less than 100 nm in thickness were amorphous at $T_s < 450$ K and contained α-Al_2O_3 at higher temperatures. In all cases, increasing the Al_2O_3 layer thickness and deposition temperature led to the formation of crystalline domains as supramolecular structures.

From the observed broadening of electron diffraction rings, the average crystallite size was evaluated to be 2 to 20 nm, depending on the layer thickness. The crystallites most likely consisted of oxide groups that had formed on periodic arrays of hydroxyl groups on homogeneous surface areas. Heat treatment of alumina layers on GaAs at 623 K considerably increased

Table 1. Oxygen-to-metal ratio in alumina layers grown at different temperatures

T_s, K	423	473	523	553	573
[O]/[Al]	4.0	2.3	1.8	1.5	1.6

Table 2. Dielectric properties of oxide nanolayers

Oxide	σ, S/cm	$E \times 10^{-6}$, V/cm	ε	tanδ
SiO_2	10^{-13}–10^{-14}	4	3.9–4.3	0.001–0.01
Al_2O_3	10^{-13}–10^{-14}	5	8–10	0.005

the intensity of the electron diffraction rings from the layers and sharply increased the crystallite size, leading to almost complete oxide crystallization. Therefore, the polycrystalline layers contained an amorphous phase between the crystallites, which was involved in the crystallization process. This conclusion is supported by the fact that the deposited films showed no preferential orientation.

The XPS spectra of the oxide layers did not show any peaks at binding energies of 190–200 or 260–270 eV, characteristic of the Cl 2*s*- and 2*p* levels. The observed broadening of the oxygen levels (530–531 eV) indicated the presence of hydroxyl groups. Note that, at oxide layer thicknesses above 8 nm (electron escape depth), the XPS spectra showed no signal from the substrate, indicating that the layers more than 8 nm in thickness were continuous.

From the peak areas for oxygen (E_b = 530–531 eV) and aluminum (E_b = 74.6 eV for Al_{2p} and E_b = 118.8 eV for Al_{2s}), we evaluated the oxygen-to-metal ratio in the oxide layers grown on GaAs at different temperatures. The results are presented in Table 1.

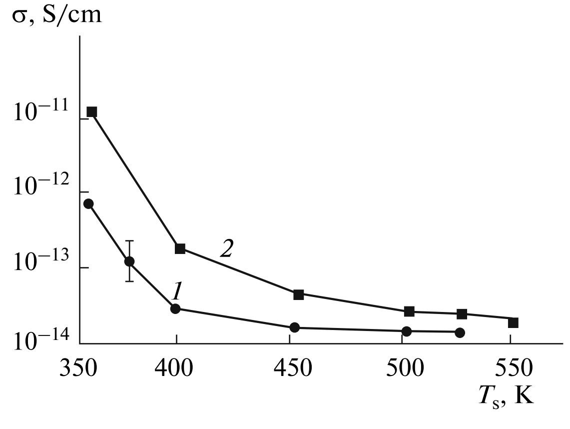


Fig. 3. Electrical conductivity as a function of deposition temperature for (*1*) SiO_2 and (*2*) Al_2O_3 layers; d = 25–30 nm, $E = 10^5$ V/cm.

It seems likely that the increased oxygen content at low and elevated deposition temperatures is due to hydration of the oxides and to the contribution of the oxide layer of the substrate, respectively.

The frustrated total internal reflection IR spectra of the alumina films grown on GaAs at T_s = 553 K on the whole correlated with the XPS results. The spectra showed well-resolved absorption peaks at ν = 744 and 835 cm^{-1}, due to Al–O bonds with the aluminum in six- and fourfold coordination [16].

The dielectric properties of the nanolayers were studied at thicknesses above 10 nm, because the electrical conductivity was then essentially independent of the layer thickness and was determined by the deposition temperature (Fig. 3). In all cases, increasing the substrate temperature reduced the conductivity to a level characteristic of layer-by-layer growth of the nanostructures. The increased conductivity of the layers at $T_s < 400$ K is most likely due to the hydration of the oxides and correlates well with the oxygen-to-metal ratios extracted from the XPS data for the layers (Table 1).

Table 2 summarizes the main dielectric properties of the oxides grown in layer-by-layer mode.

CONCLUSIONS

Silica and alumina nanolayers were grown on GaAs, InAs, and InSb substrates by ALD.

Comparison of the present experimental data with previous results for other substrate materials and other oxides [13] shows that the growth of SiO_2 and Al_2O_3 nanolayers on III–V semiconductor substrates follows the same general mechanisms, inherent in this process. In particular, analysis of the effect of deposition temperature indicates that the growth of oxide nanostructures via sequential chemisorption of metal halide and water vapors may follow three mechanisms: reaction between components in a polymolecular adsorbed layer, leading to the formation of hydrous oxides; sequential growth of monomolecular layers (layer-by-layer growth mechanism); and formation and subsequent growth of two-dimensional islands. Silicon tetrachloride chemisorption under layer-by-layer growth conditions is a thermally activated process, and layer-by-layer SiO_2 growth occurs only at $T_s > 500$ K, whereas aluminum chloride chemisorbs in the form of dimers without thermal activation. This leads to high d_0 values for Al_2O_3 at any temperature.

The dielectric properties of SiO_2 and Al_2O_3 films produced under layer-by-layer growth conditions meet the requirements for dielectric films. Therefore, the ALD process can be used to grow dielectric structures, including multilayers, for submicron-sized components of micro- and nanoelectronic systems (e.g., gate dielectrics in MIS structures), capacitors, and barrier layers.

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