

Preliminary comparison of three processes of AlN oxidation: dry, wet and mixed ones

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Three methods of AlN layers oxidation: dry, wet and mixed (wet with oxygen) were compared. Some physical parameters of oxidized thin films of aluminum nitride (AlN) layers grown on silicon Si(1 1 1) were investigated by means Energy-Dispersive X-ray Spectroscopy (EDS) and Spectroscopic Ellipsometry (SE). Three series of the thermal oxidations processes were carried out at 1012 °C in pure nitrogen as carrying gas and various gas ambients: (a) dry oxidation with oxygen, (b) wet oxidation with water steam and (c) mixed atmosphere with various process times. All the research methods have shown that along with the rising of the oxidation time, AlN layer across the aluminum oxide nitride transforms to aluminum oxide. The mixed oxidation was a faster method than the dry or wet ones.

Keywords: *thermal oxidation; AlN; Al₂O₃; AlON; EDS; SE*

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1. Introduction

III-N semiconductor compounds have been widely known for many years as a source for fabrication of many types of microelectronic and photonic devices, such as electroluminescent, laser, microwave diodes; UV photodetectors, high power transistors [1]. III-N oxides find application in contemporary microelectronics, MOS (Metal-Oxide-Semiconductors) [2–4], and MIS (Metal-Insulator-Semiconductor) [5, 6] devices for e.g. gas sensing. There are potentially many ways and means to make group III oxides [7]. The most popular are vacuum sputtering, plasma oxidation or similar techniques, however, they may damage semiconductor structures of these devices. One of the simplest methods (in terms of apparatus) is thermal oxidation of III-N which is very promising for this purpose. Determination of material parameters e.g. elements contents or refractive indices in oxidized layers is a serious problem. There is a lack of materials parameters for aluminum oxynitrides Al_xO_yN_z. Thermal oxidation of double semiconductor compounds, such as GaN or AlN is not easy

to perform: the elements – aluminum and nitrogen – can form several temporary and/or permanent stable chemical compounds with oxygen. These components differently react with oxygen and water. AlINs are thermodynamically unstable as N has a high partial pressure. Generally, in III-nitrides, oxygen substitutes nitrogen because of the high chemical affinity of aluminum, gallium or indium to oxygen but the exchange process has many steps.

2. Experimental

In all experiments epitaxial AlN layers with a thickness of about 200 nm, deposited on 2" Si(1 1 1) in Metal Organic Vapor Phase Epitaxy (MOVPE) were used. After epitaxy, the wafers were cut into 10 mm × 10 mm pieces. To remove the native oxides from the surfaces, all samples, before oxidizing, were cleaned in three steps: (a) degreasing, (b) native oxides etching and (c) purging. The samples were cleaned in TRI followed by acetone and methanol in an ultrasonic bath for 5 minutes, and then rinsed in DI water. After degreasing, the samples were rinsed in buffered (HF₂NH₄) HF for 10 minutes and then purged in DI water. Finally, the wafers were dried in compressed nitrogen N₂.

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After cleaning, the samples were placed in a quartz boat and put into the quartz reactor to thermal oxidation. A system of various time of oxidation with fixed gas flows (N_2 , O_2 , H_2O steam) was used.

To determine the parameters of obtained structures they were measured and surveyed by means of optical microscope, Energy-Dispersive X-ray Spectroscopy EDS and Spectroscopic Ellipsometry SE.

2.1. Oxidation

The samples oxidation was performed in a three-zone resistance furnace with a gas manifold (nitrogen and oxygen) and water bath. The thermal oxidation system – open chamber reactor (Fig. 1) – was described in the literature [7, 8]. All pipes and quartz tubular reactor were purged by nitrogen (with purity better than 6N). In total, the gas streams in the reactor were almost the same: ca 2 slm. In all processes, the oxidation temperature was fixed at 1012 °C.

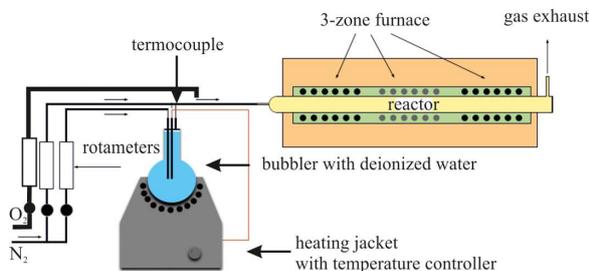


Fig. 1. Schematic diagram of the used thermal oxidation system.

Dry oxidation

The dry thermal oxidation processes of AlN were carried out in an atmosphere of a mixture of nitrogen and oxygen. The gas flow rates were kept at 1.2 slm for nitrogen and 0.75 slm for oxygen. Time of the oxidation was 10, 30, 50 and 100 minutes.

Wet oxidation

In the wet oxidation the main nitrogen flux was fixed at 1.1 slm. The second gas source was water steam from a water bubbler with hot deionized

water (96 °C). Nitrogen passing through the DI water carried the steam into the reactor with a flow rate of about 0.8 slm. The time of the oxidation was 10, 30, 50 and 100 minutes.

Mixed oxidation

N_2 was bubbled in the hot deionized water in the saturator (96 °C) and the steam were transported into the reactor. The second source of oxygen was 6N O_2 . The oxidation processes were carried out in a mixed regime that means mixed atmosphere: main nitrogen (0.9 L/min) + oxygen (0.3 L/min) + nitrogen (0.8 L/min) with a water steam from the saturator. The oxidation time was changed from 10 to 50 minutes with a step of 10 minutes.

2.2. Spectroscopic ellipsometry measurements

The optical parameters and thickness of fabricated layers of the heterostructures were measured with a V-VASE ellipsometer made by J.A. Woollam Company. The information about the amplitude ratio Ψ and phase difference Δ as a function of wavelength was obtained. The fabricated heterostructures were measured in the wavelength range of 300 to 1700 nm with a 10 nm step at three different incident angles 65, 70 and 75 degree, automatically. The mathematical model describing the heterostructure was fitted based on parameters Ψ and Δ . The optical parameters of AlN layers were approximated by the Cauchy model in order to obtain the best fit of the model. The EMA Bruggeman model [9] was used in case of composite films AlN Cauchy + % Void and Al_2O_3 + % Void. In such model, based on dielectric functions of both materials, a mathematical model is created by the fit volume fractions of components. The quality of the mathematical model fit to the data obtained by ellipsometric measurements is defined by the mean square error (MSE). The scheme of fitting the mathematical model to the results of ellipsometric measurements of the fabricated heterostructures is presented in Fig. 2.

The proposed mathematical model of the sample before oxidation (time t_0) comprises an Si substrate and AlN layer represented by an AlN layer approximated by a Cauchy model and a top thin

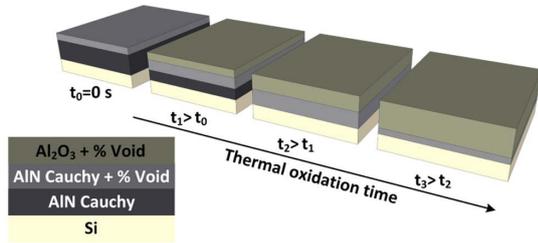


Fig. 2. Schematic view of the mathematical model system.

composite film of AlN Cauchy and various void content. The void content is a convenient way to adjust the refractive index of an analyzed layer. The time intervals t_1 , t_2 , t_3 correspond to the increasing of oxidation time. The thickness of AlN Cauchy layer decreases and the thicknesses of AlN Cauchy + % Void and Al_2O_3 + % void layers increase at the first stage of oxidation (time t_1). At the time t_2 , the AlN Cauchy layer is fully oxidized and the thicknesses of intermediate and top layers continue to grow. In the last stage of the oxidation process (time t_3), the thickness of Al_2O_3 + % Void layer increases at the expense of AlN Cauchy + % Void thickness. More detailed analysis is presented in Results and discussion section.

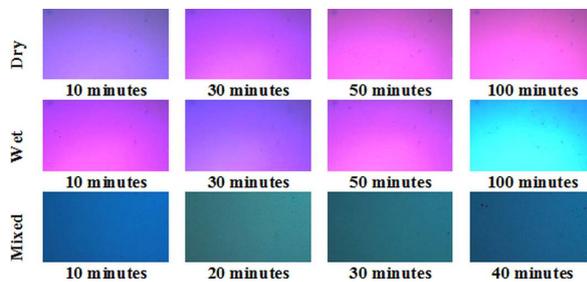


Fig. 3. Morphology of the oxidized AlN/Si surfaces.

2.3. Energy-Dispersive X-ray Spectroscopy measurements

The surface of the oxidized samples was observed by SEM Hitachi SU6600. The apparatus

has built-in EDS analyzer that was utilized to obtain quantitative results for the nitrogen and oxygen content in the structures. The signals came from K-orbit of the atoms. The device acquired the data about the contents of aluminum, nitrogen and oxygen in the samples. EDS observations of the oxidized AlN/Si samples were carried out with electron beam energy of 5 kV.

3. Results and discussion

3.1. Optical microscope survey

The surfaces of the manufactured structures were observed by means of optical microscope (Fig. 3). It is easy to notice that the colors of the surfaces are changing with the oxidation time, the oxidized layers are growing thicker.

3.2. SE measurements

The ellipsometric measurements of the AlN layers were carried out at the first step. A mathematical model, consisting of a Si substrate, AlN layer approximated by Cauchy model, a top thin composite film of AlN Cauchy and various void contents, was created (time t_0 in Fig. 2). The composite film was created by EMA (Effective Medium Approximation layer) which is an interpolation between the constituent optical constants. Bruggeman, Maxwell-Garnett or linear type theory may be used to describe the EMA. Taking into consideration the analyzed heterostructures, the Bruggeman EMA seems to be the most accurate [10]. The results of fitting mathematical model to the results obtained by ellipsometry are presented in Fig. 4.

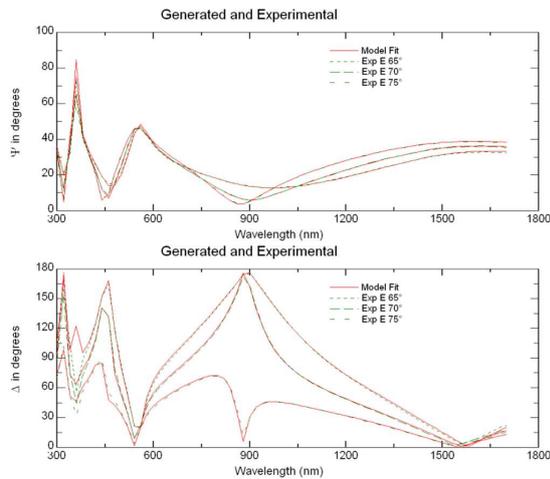
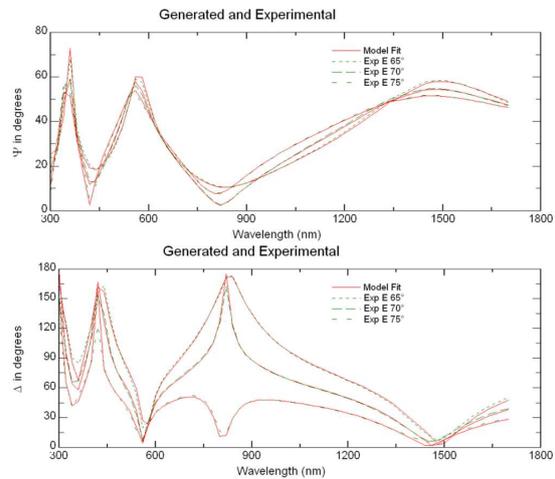
The heterostructure analyzed at the first step was thermally oxidized at different times and in three different processes: dry, wet and mixed. Consequently, Al_2O_3 layers were fabricated. The ellipsometry studies were carried out in order to obtain optical parameters and thicknesses of intermediate AlN Cauchy and top Al_2O_3 layers for each oxidation process and time. The new mathematical model includes the model created on the basis of earlier studies and top EMA of Al_2O_3 and various void contents (time intervals t_1 , t_2 , t_3 in Fig. 2). The ellipsometry database was the source

Table 1. Results obtained from SE for the oxidized structures (dry type).

Sample	Thermal oxidation time [min]	AlN Cauchy	AlN Cauchy + Void		Al ₂ O ₃ + Void		MSE
		Thickness [nm]	Thickness [nm]	Void [%]	Thickness [nm]	Void [%]	
test_aln	0	181	44	51	0	100	18.34
As33	10	154	45	12	38	44	16.13
As34	30	140	47	10	44	43	19.02
As35	50	134	48	11	45	44	19.17
As36	100	105	68	8	51	38	23.91

Table 2. Results obtained from SE for the oxidized structures (wet type).

Sample	Thermal oxidation time [min]	AlN Cauchy	AlN Cauchy + Void		Al ₂ O ₃ + Void		MSE
		Thickness [nm]	Thickness [nm]	Void [%]	Thickness [nm]	Void [%]	
test_aln	0	181	44	51	0	100	18.34
As37	10	145	41	10	40	41	16.39
As39	30	116	62	11	49	27	21.32
As38	50	78	87	9	58	19	23.93
As40	100	40	114	12	82	10	21.24

Fig. 4. Mathematical model fit to the results obtained by ellipsometry measurements: (a) amplitude ratio Ψ and (b) phase difference Δ for sample X (not oxidized AlN/Si).Fig. 5. Mathematical model fits to the results obtained by ellipsometry measurements: (a) amplitude ratio Ψ and (b) phase difference Δ for sample As19.

of optical parameters of Al₂O₃ used in the EMA model. The mathematical model fits to the results obtained by ellipsometry measurements of the sample As19 (10 minutes, mixed type of oxidation) are presented in Fig. 5.

The results obtained by the ellipsometry studies are presented in Table 1, Table 2 and Table 3.

The “X” and “test_aln” samples were the reference samples (without oxidation). The appearance of the structure presented in Fig. 2 is a result of consideration and analysis coming from computer modeling and fitting of measured ellipsometric data. We obtained the complex composite layered structures with changing thicknesses. The Tables, mentioned

Table 3. Results obtained from SE for the oxidized structures (mixed type).

Sample	Thermal oxidation time [min]	AlN Cauchy	AlN Cauchy + Void		Al ₂ O ₃ + Void		MSE
		Thickness [nm]	Thickness [nm]	Void [%]	Thickness [nm]	Void [%]	
X	0	213	62	53.1	0	100	8.62
As19	10	140	72	13.2	59	29.2	7.349
As21	20	98	93	11.2	76	19.7	13.9
As2	30	48	107	8.7	124	17.6	12.69
As22	40	0	131	7.9	165	15.8	17.1
As20	50	0	105	7.2	187	15.3	12.23

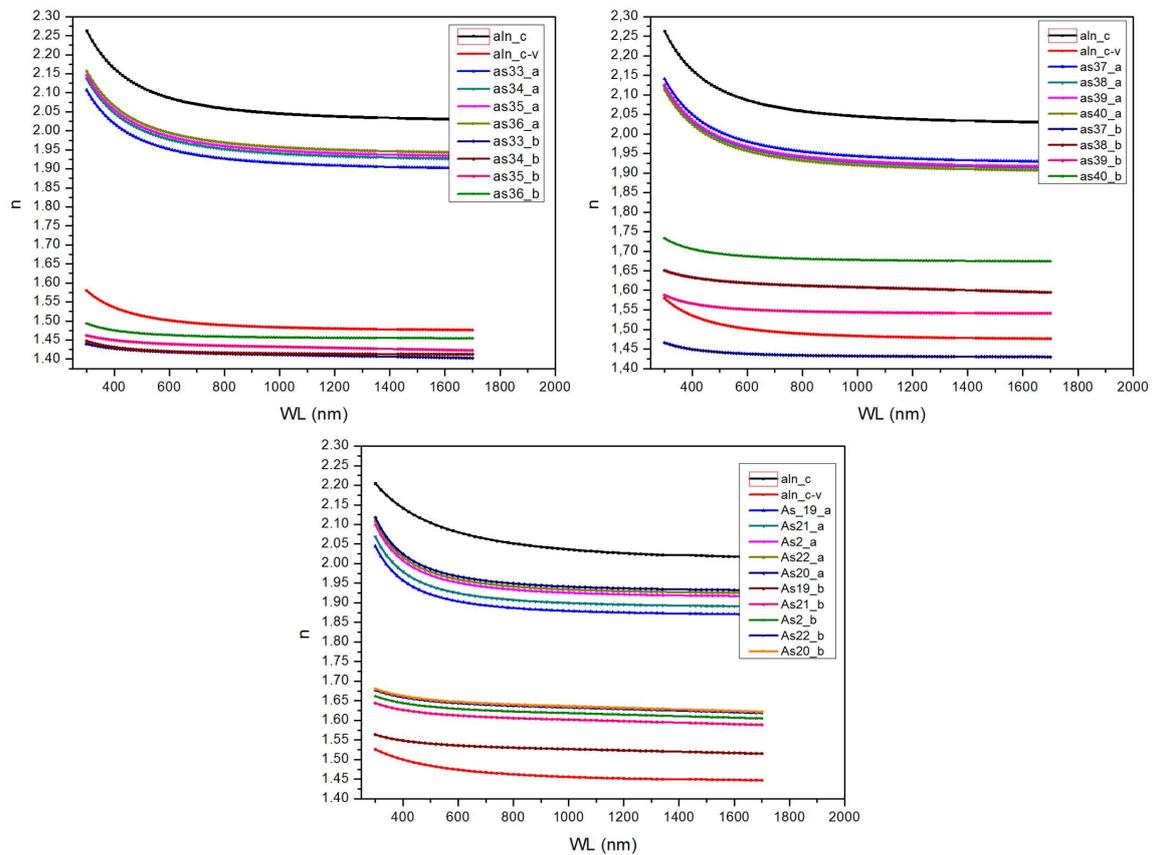


Fig. 6. Relationship between wavelength and refractive indices for all series of oxidation: (a) dry, (b) wet, (c) mixed.

above, contain the data following from modeling. “AlN Cauchy” layer is a layer of raw AlN after epitaxy, its thickness tends to zero with the oxidation time. “AlN Cauchy + Void” is called by us “infected by oxygen” AlN layer whose thickness is rising during oxidation. The third type of layer is an oxide layer “Al₂O₃ + Void”. The employed AlN/Si

structures were rather thin: there were used high temperature HT epilayers with thicknesses about 220 nm (dry and wet oxidation) and ~270 nm (mixed oxidation). They were not monocrystalline. Diffusion of oxidation agent (oxygen or/and water steam) took place through the micro cavities on the surface of AlN.

The refractive indices of all oxide composite layers for different thermal oxidation times (the data in the Table 1, Table 2, and Table 3) versus wavelength are collected in Fig. 6. In those diagrams, the curves for Al_2O_3 and composite layer $\text{AlN} + \text{Void}$ are shown. In the samples names the following extensions were used: “_a” and “_b” relating “AlN Cauchy + Void” and “ $\text{Al}_2\text{O}_3 + \text{Void}$ ” layers, respectively.

4. EDS measurements

Fig. 7 presents a typical diagram of the EDS counts. Silicon signal comes from substrate and carbon signal comes from MOVPE technology. Fig. 8 shows the atomic contents of nitrogen and oxygen in oxidized layers as a function of time of mixed oxidation. All the curves (for oxygen and nitrogen contents) can be fitted quite well by a sigmoidal function with Boltzmann model (not shown in Fig. 8).

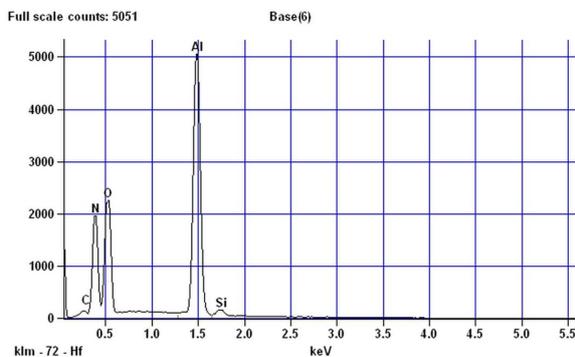


Fig. 7. EDS counts for sample As19 (oxidation time: 10 min, 5 kV).

One can observe that after 50 minute mixed oxidation, the contents of oxygen reaches the final value in Al_2O_3 of about 60 %. In addition, there is practically a lack of nitrogen.

5. Conclusions

Wet thermal oxidation of $\text{AlN}/\text{Si}(111)$ at a temperature above $1000\text{ }^\circ\text{C}$ in the presence of various gas atmospheres was studied. The experiments were carried out in dry ($\text{N}_2 + \text{O}_2$), wet ($\text{N}_2 + \text{water steam}$) and mixed ($\text{N}_2 + \text{O}_2 + \text{water steam}$)

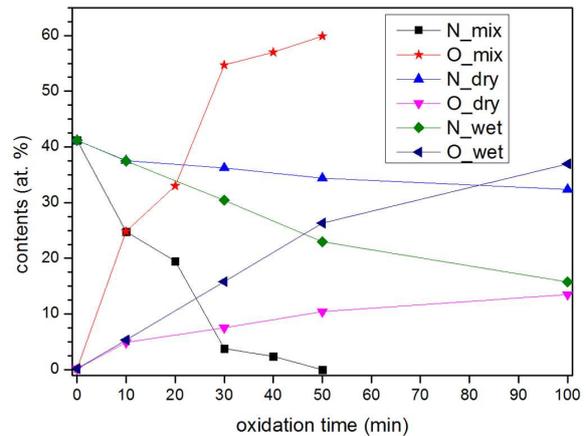


Fig. 8. Diagram of oxidation time vs. atomic contents of nitrogen and oxygen.

atmospheres. The time of the process was a variable. Simple modeling and fitting SE data gave us unsatisfactory results. We had to carry out advanced simulations to get a good match with the measured data. We have found that our oxides are not aluminum oxide Al_2O_3 but rather aluminum oxynitride with the content of oxygen in the crystal structure dependent on the time of the oxidation process and on the type of the oxidation (dry, wet, mixed). The obtained structures were complex and consisted of three layers: AlN, AlN “infected” by oxidation agent (O_2 or/and H_2O) and oxide layer Al_2O_3 . Our observations show that mixed oxidation is the most effective method for production the oxidized AlN layers.

The data obtained by us indicate the need for detailed analysis of the AlN oxidation process, especially the influence of the atomic hydrogen, which will be made in the next paper.

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