THIN AlN FILMS GROWTH ON Si (III) BY HYDRIDE VAPOR PHASE EPITAXY

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Thin AlN layers have been grown on Si (111) by hydride vapor phase epitaxy (HVPE) method in a horizontal quartz reactor. The surface of layers has been studied by scanning electron microscopy and by the Raman spectroscopy method and found to have the structured morphology. It has been determined that the layers have high specific electrical resistance and are strained in the plane of the substrate.

1. Introduction

GaN and related compounds have attracted interest because of their applications in short-wavelength emitting diodes and lasers, detectors as well as in high-temperature, high-frequency, and high-power electronics. Most of III-nitride materials and devices were obtained on sapphire or silicon carbide substrates – materials with high cost and of rather deficiency. Other materials are investigated as substrates; however, the rigid technological requirements (heats, chemical aggressive media, etc.) have sharply reduced the number of suitable substances. Recently, a special attention has been given to silicon for using as a substrate. This material has a heat of fusion; it is thermodynamically stable at heats; it has crystallographic planes with trigonal symmetry, and is rather cheap and accessible. Moreover, integration of the nitride technologies with silicon would also have an essential economic impact. Obtaining of an epitaxial layer of gallium nitride directly on silicon encounters a series of obstacles: formation of eutectic drops Ga - Si and erosion of the surface of substrates, as a result of interaction of the Si with GaN and formation of amorphous Si_xN_y, a significant mismatch of silicon and gallium nitride to the parameters of a crystalline lattice and coefficients of thermal expansion. Overcoming of these obstacles would allow designing of semiconductor devices on the basis of 111 nitrides on silicon. Partly, they can be overcome by means of intermediate buffer layers disposed on interface stratum - substrate. A suitable material for buffer layers is aluminum nitride. Some aspects of a deposition of aluminum nitride on silicon by MBE (molecular-beam epitaxy), MOCVD (metal organic chemical vapor deposition), and HVPE methods are reviewed in [1].

2. Experimental

The present work is concerned with studying of some physical properties of aluminum nitride layers grown on silicon by the HVPE method. The AlN layers were obtained by chemical transport reactions method in a horizontal quartz reactor. As a transport gas, hydrogen cleaned by a palladium filter was utilized. Ammonia, chloride hydrogen, and aluminum (cleanness grade 6N) were used as reagents. Substrates of 2 inches in diameter were etched in standard silicon enchants with immediate introduction into the reactor. The thermal field in

the reactor was provided by means of a resistive heater. The temperature of aluminum source during growth was 850°C. The growth of layers was carried out in a temperature interval 700-1200°C. During the deposition of the layers, the substrates were rotated by stream of hydrogen with a frequency of 50-100 rpm. The general charge of hydrogen was 4.8 slpm; ammonia, 2.4 slpm; and hydrogen chloride, 5 smlpm.

3. Results and discussion

The AlN films grown on silicon are smooth, shining, and mirror-like. On some of them, being thinner, concentric interference bands of ~10 mm in width of red-cherry ($\lambda_r \sim 760$ nm) and green ($\lambda_g \sim 527$ nm) colors are observed. The thickness of bands change on the surface is wedge-shaped. They can be estimated by the formula $d = \lambda\, k/2n$, where λ, $k = 1$, and $n = 2.15$ are the wave length of the maximal intensity, order of interference bands, and the refractivity, respectively. In the center of substrates $d_c = 760/2{\cdot}2.15 = 177$ nm, and on periphery $d_p = 527/2{\cdot}2.15 = 122$ nm (average thickness of the obtained sample $d \sim 150$ nm). The change in the thickness of AlN band on the surface is also confirmed by the investigation of breakdown voltage of structures. In the center it reaches 400 V; on edges, 300 V (the average value on the entire surface of the layer is ~ 350 V). The average value of the breakdown voltage is ~ 350V/150 nm = 23 MV/cm, a magnitude characteristic of dielectrics. The avalanche-type breakdown voltage for silicon with a specific resistance of 4.5 Ω·cm and an impurity concentration of 10^{15} cm^{-3} is ~100 V [2]. Therefore, the voltage drop on the AlN layer does not exceed 250 V, and, accordingly, the breakdown voltage of the field is less than 17 MV/cm. It should be noted that for bulk AlN (6.2 eV) at 300°C the shorting electric field strength is ~1.2-1.8 MV/cm; for SiO_2, ~1 MV/cm.

The surfaces of layers have been studied by scanning electron microscopy (SEM). The morphology of the surface of one specimen, obtained at 1100 C during 10 minutes, is presented in Fig. 1. The surface is structured, and this is more precisely observed in the inverted image (Fig. 2). The layers obtained at identical requirements, but at different temperatures (800, 900, 1000, 1200°C), have similar structures of the surface. Figure 3 presents the SEM image of the cross-section structure of AlN/Si (111). Silicon is in the bottom of the figure. The layer of AlN with the thickness ~1 μm is organized by structured blocks. The upper edge of the layer AlN is hilly that correlates with a contour of a surface of the layer presented in Figs. 1 and 2.

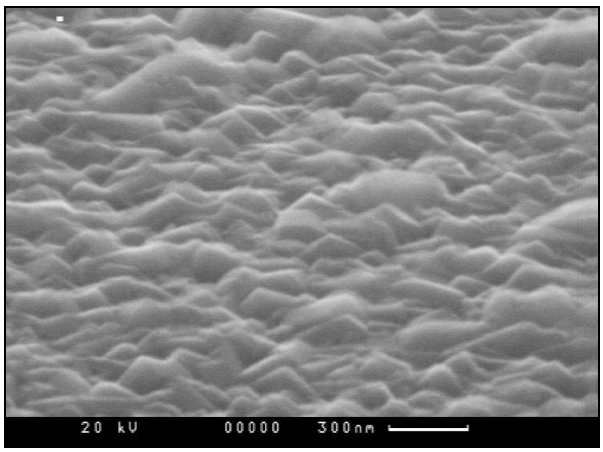


Fig. 1. Image of the surface of the AlN layer grown on Si (111), obtained by SEM.

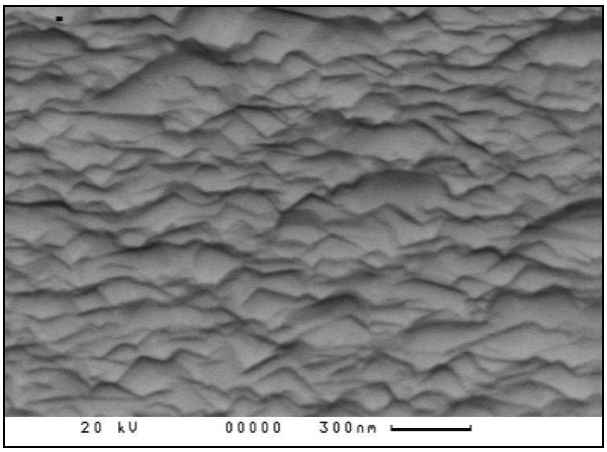


Fig. 2. Inverted image of the surface of the AlN layer grown on Si (111), obtained by SEM.

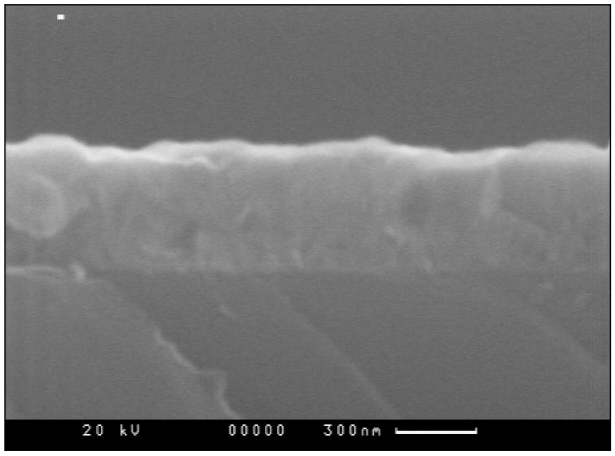


Fig. 3. SEM image of the cross-section of the structure AlN/Si (111).

Properties of AlN/Si layers have also been investigated by the Raman spectroscopy method. Analytical potential of this method for the characteristic of structures on the basis of 111-nitrides is based, mainly, on measurements of half width of phonon lines of dispersion, determining the positions of these lines in the energy spectrum. These parameters provide the information on the quality of layers, and also on the size of residual stresses in them. Raman spectrum of AlN with hexagonal structure contains 6 optical phonon branches. Each branch can be studied in the fixed geometrical configuration, which is determined by the relative position of the wave vector and the polarization vector of incident wave and the crystallographic axis C_6 of the layer.

Usually, for the characteristic of layers, the phonon branch E_2 (high) is studied more often. Its half-width is highly sensitive to presence of structural defects, and its arrangement in the energy spectrum determines the character of mechanical strain (a stretching or compression) in samples.

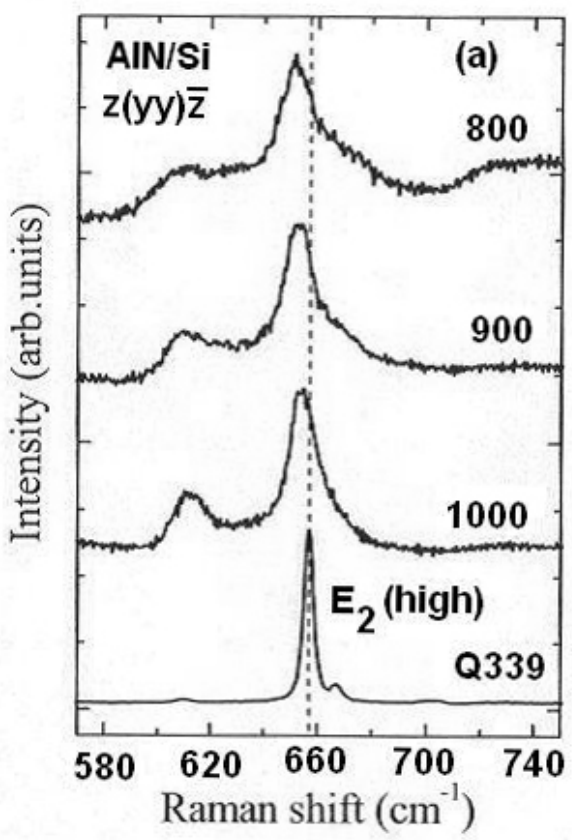


Fig. 4. Raman spectra obtained at 300 K for the layers AlN/Si (111) grown at 800, 900, and 1000°C. The spectrum Q339 belongs to the undistorted AlN layer (d = 5 μm) grown by the MOCVD method, it is given as a standard. The wave vector of incident beam is parallel to the axis C_6 of the layer. The geometry used in the research is shown in the figure.

In Fig. 4, the Raman spectra of AlN layers grown on Si (111) in a temperature interval of 800-1000°C with duration of 10 minutes, for the phonon branch E_2 (high), are presented. In the figure, the spectrum of the standard AlN sample obtained by the MOCVD method on sapphire is also presented. In figure 4 we show the dependence of some parameters of layers on growth temperature. The full width at half-maximum (FWHM) of the phonon branches E_2 (high), their position in the energy spectrum of the samples obtained in a temperature interval of 800-1100°C with duration of 20 minutes are listed in the table below.

Table. Parameters obtained from the Raman spectra.

#	ω,cm^{-1}	Δω, FWHM, cm^{-1}	$\delta_{xx,\ Gpa}$
800	652,6	25,5	1,3
900	652,5	22,3	1,33
1000	652,8	10,3	1,24
1100	652,5	11	1,33
Q339	657	3,5	0

Figure 5 presents the temperature dependences of parameters of AlN layers grown on silicon in identical technological conditions, but at smaller duration of propagation, 10 minutes.

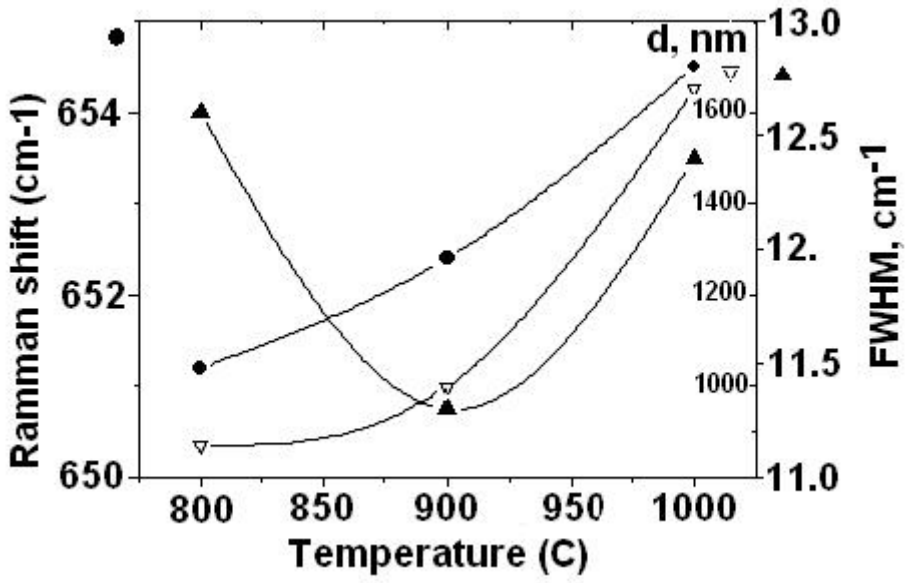


Fig. 5. Dependences of Raman shift, the full width at half-maximum (FWHM) and thickness (d) of the AlN layers grown on Si (111), duration of 10 minutes.

From the table and Fig. 5, one can notice that the position of the maximum of lines on the energy scale depends on the duration of growth of layers. For samples grown for 20 minutes, the position of the maximum with temperature does not vary. At the growth duration of 10 minutes with rise in temperature the maximum is displaced aside arrangements of the maximum of the undistorted (reference) sample. At both durations of growth, the FWHM changes with temperature pass through the minimum in a range of 900-1000°C. It is apparent that this phenomenon is a result of the silicon surface reorganization occurring in this interval of temperatures.

It is known that the size of FWHM is inversely proportional to the life time of the phonon, which in its turn is determined by the concentration of defects. For the most qualitative

samples the size of FWHM with symmetry E_2 is in a range of 3 - 3.5 cm^{-1}. From the table and Fig. 5, it is seen that this value for the most qualitative layers is on the order of 10 cm^{-1}. This shows the presence of structural defects in the obtained samples.

From Fig. 4, it is seen that the position of the peak of the line E_2 of grown layers is displaced towards smaller frequencies in comparison with the position of the reference peak of the undistorted sample. This displacement specifies the presence of pressure of stretching in the plane of the substrate. The different size of the displacement testifies that the residual size of deformations in layers depends on temperature and duration of growth. The presence of pressure of stretching in the layers denotes a mismatch of silicon and aluminum nitride to the parameters of crystal lattices (a_{AlN} = 3.12 A and $a_{Si(111)}$=3.82 A) and the coefficient of thermal expansion ($\alpha_{AlN} = 4.15 \cdot 10^{-6}$ K^{-1} and $\alpha_{Si} = 2.6 \cdot 10^{-6}$ K^{-1}).

The size of residual deformation in the plane of the substrate in the model of biaxial deformations has been estimated considering that Raman displacement for branch E_2 (high) is proportional to the size of the deformation, $\Delta\omega_\gamma = K_\gamma . \delta_{xx}$, [3]. The value of the linear factor of deformation, K_γ, for AlN is taken from [4]. The results of calculations are listed in the table.
The presence in the Raman spectrum of the AlN layers of a band with a wave number of ~610 cm^{-1} can be caused by noncompliance with the selection rules at photon - phonon interaction due to the polycrystalline character of layers.

4. Conclusions

The AlN layers on Si (111) can be synthesized by the HVPE method in a horizontal quartz reactor. They have the structured morphology; they are dielectrics and are strained in the plane of the substrate.

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References

[1] S. Raevschi, Yu. Zhilyaev, L. Gorceac, P. Gaugas, and V. Botnariuc, Epitaxia nitritului de galiu pe siliciu prin metoda HVPE, Analele stiintifice ale Universitatii de Stat din Moldova, seria ”Stiinte fizico-matematice”, Chisinau, CEP USM, 19, (2006).
[2] S.M. Sze, Physics of Semiconductor Devices, M., Mir, 456, 1984.
[3] V.Yu. Davydov, N.S. Averkiev, I.N. Goncharuk, D.K. Nelson, I.P. Nikitina, A.S. Polkovnikov, A.N. Smirnov, M.A. Jacobson, and O.K. Semchinova, J. Appl. Phys., 82, 10, 5097, (1997).
[4] M. Kuball, J.M. Hayes, A.D. Prins, N.W.A. van Uden, D.J. Dunstan, Y. Shi, and J.H. Edgar, Appl. Phys. Lett., 78, 724, (2001).