Pulsed laser deposition of aluminum nitride nanowires

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Abstract. The possibility of AlN nanowires deposition on single-crystal silicon substrates by pulsed laser deposition in vacuum is shown in this work. Experimental samples were investigated by scanning electron microscopy and infrared Fourier spectroscopy. It is shown that the possible mechanism for the AlN nanowires formation is the "vapor-liquid-crystal" mechanism.

1. Introduction
A combination of outstanding properties of aluminum nitride, such as a large band gap (6.2 eV), high thermal conductivity (320 W/(m·K) at 300 K), high breakdown field strength (17 kV/mm) and the ability to form a continuous series of AlN - GaN solid solutions, predetermined its wide use in devices of high-power microwave electronics and optoelectronics. The AlN-GaN heterocompositions obtained by molecular-beam epitaxy or gas-phase epitaxy are actively applied for the creation of transistors with 2D electron gas [1], UV light emitting diodes and lasers [2, 3]. In addition, thin AlN films are applicable as dielectric, passivating and heat-conductive layers [4, 5]. However, the most promising structures based on AlN with unique transport, luminescence and adsorption properties today are nanoscale whiskers – a new class of materials for future nanoelectronics and sensors [6, 7]. Therefore, the aim of this work was to study of possibilities of AlN nanowires synthesis on silicon substrates by pulsed laser deposition (PLD).

2. Experiment
Experimental samples of AlN layers were obtained by PLD method from a ceramic AlN target (99.5%) of stoichiometric composition using an excimer KrF laser (laser radiation wavelength 248 nm, pulse duration 20 ns, pulse repetition rate 15 Hz) under high vacuum (3 × 10⁻6 Torr). Monocrystalline silicon wafers with a diameter of 50 mm and (100) orientation were used as substrates. The samples were grown at substrate temperatures of 600, 700, and 800°C. The substrate heating was carried out by an IR oven. The temperature monitoring was carried out by means of thermocouple and pyrometer. The uniformity of heating was ± 6 °C on all area of a growth surface.

3. Results and discussion
The morphology of a surface of experimental samples was investigated by means of scanning electron microscopy (SEM). Figure 1 shows the SEM images of the planar surface of structures obtained at substrate temperatures (t_{sub}) of 600°C (a), 700°C (b), and 800°C (c). The surface of the sample grown at t_{sub} = 600°C in vacuum (Figure 1, a) is relatively smooth and covered with microdroplets whose
diameter fluctuates in the range from 20 to 200 nm, and the surface concentration reaches values of \( \sim 10^3 \, \mu m^{-2} \). The presence of such particles is typical for the films formed by PLD method. Physical mechanisms contributing to the particulates formation are splashing of the molten surface layer caused by surface boiling, expulsion of the liquid layer by shock waves.

![Figure 1](image1.png)

**Figure 1.** SEM images of experimental samples deposited at the following substrate temperatures: (a) – 600°C, (b) – 700°C, (c) – 800°C.

In turn, the surface morphology of the sample grown at \( t_{\text{sub}} = 700°C \) changes drastically (Figure 1, b). The formation of an array of disordered nanowires with a diameter of 35 – 50 nm and a length up to 0.5 \( \mu m \) is observed at this temperature. Also a growth of multiple nanowires from one basis is observed. Nanowires uniformly cover the entire surface of the sample, and there are crystallized droplets in the form of hemispheres at their ends. An increase in \( t_{\text{sub}} \) up to 800°C leads to an increase of the nanowires diameter and to decrease in their surface density (Figure 1,c).

In figures 2,a and 2,b the SEM images of the cross section of the samples deposited under the substrate temperatures of 600°C and 700°C are shown. It can be seen from these figures that the film thickness for the sample without AlN nanowires is about 100 nm. The height of the nanowires formed on the surface of the sample at 700°C reaches a value of 400 nm (Figure 2,b), and the crystallized droplets at the ends of the nanowires sometimes have a slightly pronounced facet (Figure, 2c).

![Figure 2](image2.png)

**Figure 2.** SEM images of the cross-section of samples deposited at substrate temperatures of: (a) – 600 °C, (b) – 700 °C; (c) – SEM image of individual AlN nanowire.

An array of oriented AlN nanowires of similar dimensions (with a diameter of 50-60 nm and a length of about 250 nm) were obtained by molecular beam epitaxy [8] on a single-crystal silicon substrate. However, the mechanism of formation of such nanowires in [8] is not disclosed.
In order to evaluate the composition and structural features of the formed layers, spectra of their transmission in the IR region were obtained (Figure 3, a). Measurements of the transmission spectra were carried out by 8400S (Shimadzu) FTIR spectrometer using standard technique with a resolution of 2 cm\(^{-1}\). It can be seen from Figure 3a that the spectra of experimental samples deposited at substrate temperatures of 700 and 800°C contain one broad absorption band in the range of 400 – 1000 cm\(^{-1}\), which can be associated with the vibrational modes of the AlN lattice [9]. Moreover, as the \(t_{\text{sub}}\) parameter increases, the intensity of this band increases, and its half-width decreases from 200 cm\(^{-1}\) (at \(t_{\text{sub}} = 700°C\)) to 130 cm\(^{-1}\) (at \(t_{\text{sub}} = 800°C\)). The decrease in the half-width of the absorption band with increasing temperature is associated with an improvement in the crystallinity of the layers being formed. In turn, the sample obtained at 700°C demonstrates strong absorption in the entire measured spectral range, which is probably related to the accumulation of metal (Al) in its volume.

**Figure 3.** IR-transmission spectra of experimental samples (a). The result of decomposition of the absorption spectrum for the sample deposited at 800°C (b).

For the sample deposited at 800°C, the transmission spectrum \(T (%)\) was recalculated in the spectral distribution of an absorption coefficient \(\alpha (\text{cm}^{-1})\) followed by the decomposition of the integral spectra into two Gaussian components (Figure 3, b), the parameters of which are presented in Table 1. According to literature data, the transverse optical phonon mode of AlN (TO) lies in the range of 660 – 670 cm\(^{-1}\), the longitudinal optical modes of AlN (LO) are in the range of 880 – 915 cm\(^{-1}\) [10, 11]. Thus, the first peak with \(\omega_{\text{max}} = 674 \text{ cm}^{-1}\) can be attributed to the TO vibration mode of Al-N bonds. However, the second peak with \(\omega_{\text{max}} = 855 \text{ cm}^{-1}\) is located in the range between TO and LO modes. This peak can be associated with the appearance of surface modes of optical oscillations (SO) at crystallite sizes less than the wavelength of incident light [10]. The observed size effect confirms formation of AlN nanowires.

| Peak № | Peak position, cm\(^{-1}\) | Peak half-width, cm\(^{-1}\) | Intensity, rel. units | Description               |
|--------|-----------------------------|-----------------------------|----------------------|---------------------------|
| 1      | 674                         | 146                         | 26                   | TO – transverse optical phonon mode of AlN |
| 2      | 855                         | 156                         | 7                    | SO – surface optical mode of AlN NW |

The possible mechanism for the AlN nanowires formation is the "vapor-liquid-crystal" (VLS) mechanism. Excess Al accumulates on the growth surface during the formation of the AlN layer under...
vacuum. This excess Al is collected to the nanodroplets, which react with the substrate dissolving silicon in its volume. Then Al-Si melt is acting as a catalyst for the growth of nanowires [12]. The presence of crystallized droplets at the ends of whiskers and the absence of nanowire at $t_{\text{sub}} = 600^\circ$C (that is lower than temperature of Al melting) confirm this assumption.

4. Conclusion

The samples containing arrays of the disordered AlN nanowires on single-crystal silicon substrates were obtained at $t_{\text{sub}} = 700$ and 800°C by PLD method. The experimental samples were investigated by scanning electron microscopy and infrared Fourier spectroscopy. It is shown that the possible mechanism for the AlN nanowires formation is the "vapor-liquid-crystal" (VLS) mechanism. This work was carried out using the equipment of MEPhI Shared-Use Equipment Center «Heterostructural microwave electronics and wide band gap semiconductor physics».

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