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FABRICATION, TREATMENT, AND TESTING OF MATERIALS AND STRUCTURES

On a Reduction in Cracking upon the Growth of AlN on Si Substrates by Hydride Vapor-Phase Epitaxy

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Abstract—The main problem of the epitaxial growth of thick AlN layers on a Si substrate consists in the formation of cracks, which complicates the application of structures of this kind in the fabrication of semiconductor devices. The possibility of obtaining crack-free AlN layers with a thickness exceeding 1 μm and a mirror-smooth surface by hydride vapor-phase epitaxy is demonstrated. The properties of the layers are studied by X-diffraction analysis, optical and scanning electron microscopy, and Raman spectroscopy.

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1. INTRODUCTION

Aluminum nitride (AlN), a direct-gap semiconductor with wide band gap ($E_g = 6.2$ eV), is promising for the development of ultraviolet (UV) light-emitting diodes, photodetectors, acoustoelectric devices, high-electron-mobility transistors, and a multitude of other applications. Because of the high cost and the fact it is difficult to obtain bulk crystals and wafers of AlN, the heteroepitaxial growth of AlN films on substrates of other materials, such as silicon carbide (SiC), sapphire (Al_2O_3), and silicon (Si), is widely used. As regards its physical properties, SiC is the most suitable material for the heteroepitaxial growth of AlN layers because it has a small lattice mismatch with AlN (~1%), high thermal conductivity, and chemical stability at high temperatures. However, the wide use of SiC substrates is hindered by their high cost. A possible alternative in this case is silicon, which is increasingly used at present in devices of nitride electronics to reduce production costs. The cost of silicon substrates is nearly an order of magnitude lower than that of sapphire substrates and two orders of magnitude lower than that of SiC substrates. In contrast to insulating sapphire substrates, the electrical conductivity of silicon substrates can be widely varied by doping. The thermal conductivity of silicon is six times that of sapphire, but three times lower than that of SiC. In addition, it should be noted that obtaining high-quality AlN epitaxial layers on Si includes a number of technological difficulties. The large lattice mismatch (19%) and noticeable difference between the thermal-expansion coefficients of AlN and Si lead to high mechanical stresses and cause the cracking of layers with an increase in their thickness, and just for this reason most previously published studies of AlN epitaxy on Si are concerned with the growth of thin (< 1 μm) layers [1–6]. As reported in [2], AlN films are highly susceptible to cracking even at thicknesses of 300 nm, with stresses of ~0.26–0.56 GPa developing in these films. The development of a technique for the deposition of high-quality AlN layers onto Si substrates is of significant practical and scientific interest.

Several approaches to improving the quality of AlN layers on Si substrates have been suggested previously. The use of AlN/AlGaN superlattices leads to the relaxation of stresses at the heterointerface and reduces the dislocation density. Approximately the same approach has been tested in the growth of gallium nitride, with MOCVD grown AlN serving as a buffer layer [7]. The density of threading dislocations can also be effectively lowered by using the epitaxial lateral overgrowth (ELOG) technique and by selecting the growth conditions in the initial stage of layer formation [8]. It was shown in [9, 10] that the quality of AlN layers is improved if an intermediate 3*C*-SiC layer is deposited between AlN and Si (111). In the present study, we examine the possibility of obtaining thick crack-free AlN layers on silicon substrates without the use of additional buffer layers.

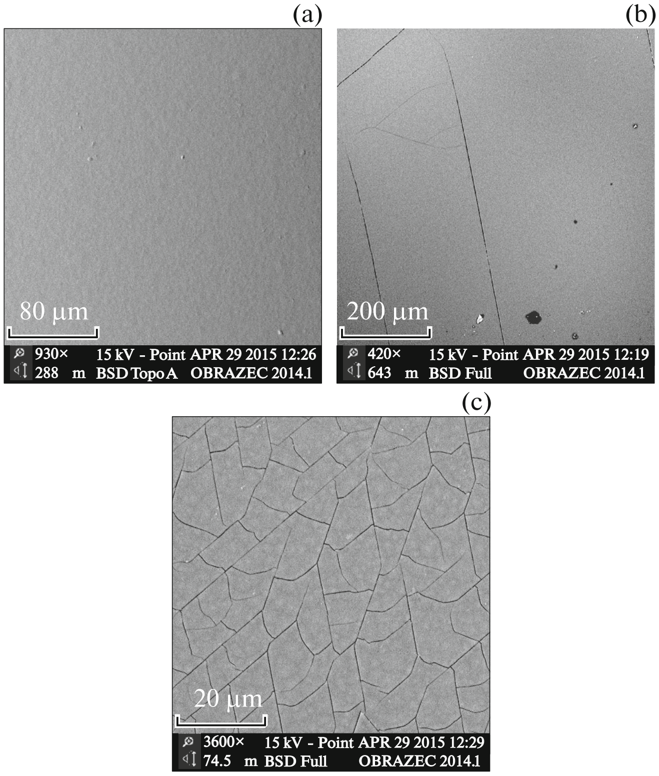

Fig. 1. SEM images of AlN layers on a Si (111) substrate, depending on the pregrowth-treatment conditions and growth temperatures: (a) chemical treatment, T_g = 1130°C; (b) chemical treatment, T_g = 1050°C; (c) no chemical treatment, T_g = 1050°C.

2. EXPERIMENTAL

Epitaxial layers of aluminum nitride were grown by hydrogen vapor-phase epitaxy (HVPE) in a horizontal reactor. An AlN film was deposited as a result of a gas-phase reaction between aluminum trichloride ($AlCl_3$) and ammonia (NH_3). Aluminum trichloride was synthesized directly within the reactor by passing gaseous hydrogen chloride over metallic aluminum. Argon (Ar) served as the carrier gas. The temperature at the aluminum source was 550°C, and that in the growth zone, T_g = 1130°C, with the pressure in the reactor being close to that in the atmosphere. Si (111) substrates were used in the experiments. An important role in obtaining high-quality AlN layers on Si is played by the order in which substrates are washed and prepared before growth. The Si substrates were washed with isopropanol at a temperature of 80°C for 20 min. Then, the substrates were submerged in an aqueous solution of hydrofluoric acid ($5H_2O$:2HF) for 2 min. After that the substrates were loaded into the reactor and blown with a flow of argon, with the reactor gradually heated to the growth temperature. After this temperature was reached, $AlCl_3$ was supplied to the growth zone to saturate the Si surface with aluminum and preclude the formation of SiN_x. The supply of NH_3 was switched on with a delay of 30 s, and AlN started to be deposited. Growth continued for 15 min at a rate of about 0.1 µm/min. To verify the reproducibility of the results, a set of similar growth experiments was performed. The measurement results demonstrated an insignificant scatter of the physical parameters of the resulting samples.

The surface morphology was examined by scanning electron microscopy (SEM) using a JSM-7100F microscope. The crystal perfection of the AlN layers on Si was examined by means of X-ray diffraction analysis. The Raman spectra were measured by a Horiba Jobin Yvon T64000 spectrometer device at room temperature. The device was equipped with an Olympus BX41 confocal microscope, which made it possible to focus the laser beam into a spot 1 µm in diameter. The spectra were recorded with a CCD–1024 × 256–Open-3LD CCD array cooled with nitrogen. The Raman spectra were excited with a Nd:YAG continuous-wave solid-state laser with diode pumping (λ_{ex} = 532 nm). The spectra were calibrated against the line of a Si (111) test sample.

3. RESULTS

With the growth parameter chosen in the optimal way, we obtained crack-free AlN layers on a large-area substrate. The layers were transparent and had a smooth morphology (Fig. 1a). For this purpose, we treated the substrate surface in an acid solution to remove the oxide SiO_2 from the substrate. The best result was obtained at a growth temperature of 1130°C. Figure 1b shows a layer grown on a Si substrate under the same conditions, but at a lower growth temperature T = 1050°C. Figure 1c shows a layer grown on a substrate not subjected to chemical treatment. The full width at half-maximum (FWHM) of the rocking curves for the best samples (as those in Fig. 1a) was ω_θ ~ 29 arcmin (Fig. 2), which is markedly better than the values reported for HVPE-grown AlN layers in [3].

Figure 3a shows the polarized Raman spectra of AlN/Si(111) layers, measured in the backscattering geometry $z(xx)\bar{z}$ at different points of the sample: at the center (p.1) and on the periphery (p.2) of an AlN block (see Fig. 3b). Here, direction z coincides with the growth direction of the AlN layer, and direction x lies in the substrate plane. The AlN layers are transparent to the excitation light (λ_{ex} = 532 nm), and, therefore, the Raman spectrum recorded from the sample surface shows at the given AlN layer thickness (~1 µm) bands from both the AlN layer and Si (111) substrate. The spectra contain bands that can be attributed to scattering in the AlN layer on (E_2 (low), E_2 (high), and A_1(LO) symmetry phonons, which agrees with selection rules for crystals with the wurtzite structure [11, 12]. Based on the Raman spectroscopic data, we can state that the hexagonal axis of the

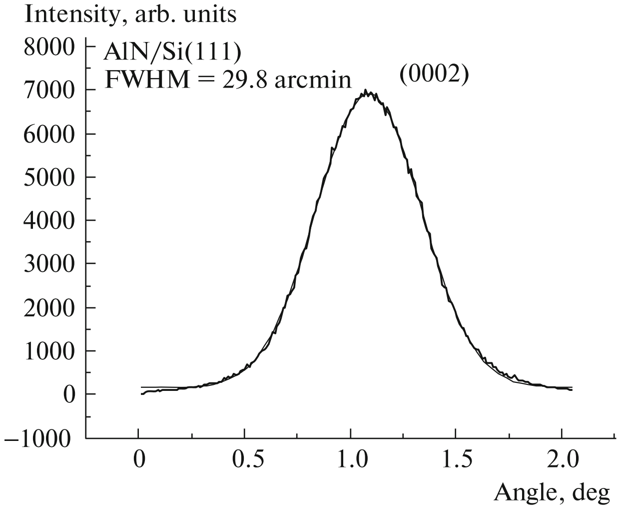

Fig. 2. X-ray rocking curve for the AlN layer grown on Si (111).

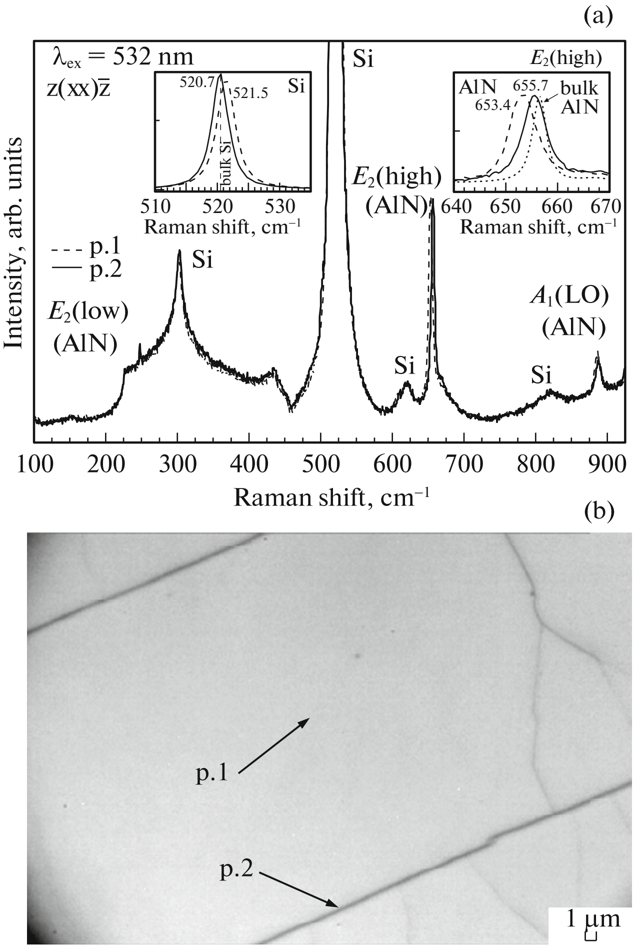

Fig. 3. (a) Raman spectra of the AlN/Si (111) sample, measured at different points (p.1 and p.2). The insets show the spectra in the ranges of the phonon line of silicon (left-hand) and E_2 (high) symmetry phonon line of aluminum nitride (right-hand). (b) Optical image of the region from which the Raman spectra were obtained.

AlN layers is directed perpendicular to the substrate plane.

The right-hand inset in Fig. 3a shows the spectra obtained at two points of the AlN layer under study in the range of the E_2 (high) symmetry phonon and also the spectrum of bulk (unstrained) AlN. It can be seen that the frequency position of the band associated with the E_2 (high) symmetry phonon is shifted for both points to lower frequencies relative to the position of this band in bulk AlN. This shift is due to the presence, in the layer under study, of tensile elastic stresses in the plane perpendicular to the growth direction of the AlN layer. Using data on the deformation-potential constants of phonons in AlN [13], we calculated the stresses in the AlN layer plane (σ_{xx}) to be +0.50 GPa at the center of the block and +0.14 GPa at its periphery.

It should be noted that elastic strains are also present in the interfacial Si layer (at the center of the block), but these strains are compressive in the substrate plane, which is evidenced by the fact that the phonon line of Si is shifted to longer wavelengths relative to its position in bulk Si (left-hand inset in Fig. 3a).

4. CONCLUSIONS

It was shown that high-quality thick (>1 μm) crack-free aluminum-nitride layers can be, in principle, formed by hydride vapor-phase epitaxy on silicon substrates. The stresses in the plane of the AlN layer (σ_{xx}), at which cracks may appear, and the degree of relaxation of these stresses upon crack formation were determined. With the silicon surface pretreated and growth conditions chosen, AlN layers with a full width at half-maximum of the X-ray diffraction rocking curves of about 29 arcmin were obtained, which is comparable with the results obtained on sapphire and silicon-carbide substrates. The layers can be used to develop various electronic devices as, e.g., an insulating layer in high-voltage AlGaN/GaN high-electron-mobility transistors.

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