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Investigation of Textured Aluminum Nitride Films Prepared by Chemical Vapor Deposition

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Abstract—Textured polycrystalline aluminum nitride films are grown on a silica substrate by chemical vapor deposition using metallic aluminum and ammonium chloride as the initial reagents. The good texture and crystal quality of the prepared films are confirmed by raster electron microscopy, Raman spectroscopy, and X-ray diffraction.

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INTRODUCTION

Aluminum nitride holds a unique position among the semiconductors of the $A^{III}B^{V}$ type. It possesses a unique combination of valuable properties, among which a particularly broad bandgap width (6.2 eV) and the ability to undergo *n*- and *p*-doping, high piezoelectric and dielectric characteristics, high heat conductivity, and heat and chemical stability can be highlighted [1]. Due to this aluminum nitride is promising for the application in various devices such as electroacoustic transducers [2], sources of radiation in far-UV range and short-wave lasers [3], and UV detectors [4]. Because the growth of AlN monocrystals is associated with remarkable difficulties [5], the works on the preparation of high-quality aluminum-nitride films on various substrates [6, 7] are of great interest. Due to the absence of the central symmetry in the wurtzite crystal structure, some properties of AlN films such as spontaneous and piezoelectric polarization along the *c* crystallographic axis depend significantly on the texture [8]. Therefore, the good texture of the films, along with a high crystal quality is a core requirement for some practical applications. In this work, the possibility of the preparation of textured aluminum nitride films on a silica substrate using our recently developed simple type of chloride-hydride method of chemical vapor deposition of AlN was considered [9].

EXPERIMENTAL

In order to grow AlN films, a tubular quartz reactor with three heating zones with various temperatures was used. The given temperature in the zones was maintained by external tubular resistance-type heaters. A silica boat was placed inside the reactor, where the mounting with substrates, a rod made from metallic aluminum, and a container with a shot of ammonium chloride were placed successively at a particular distance from each other. The boat was placed in such a way that the substrates, metallic aluminum, and ammonium chloride would appear in different heating zones. The process occurred by the following scheme. Heating ammonium chloride led to its sublimation. The products of sublimation (NH_3 and HCl) reacted with it to give aluminum chloride monoammine ($AlCl_3NH_3$) after passing the surface of heated aluminum. The vapors of the latter were transferred by the argon flow to the high-temperature zone, where the pyrolysis of $AlCl_3NH_3$ led to the formation of aluminum nitride.

As the initial components, metallic aluminum (99.99%) and ammonium chloride (OSCh 4–5) preliminarily dried over P_2O_5 were used. Ultrapure nitrogen (of the PNG brand) acted as the carrier gas. As substrates, silicon (100) was used. The nitrogen flow supplied to the reactor corresponded to 0.7 L/min. The consumption of ammonium chloride was set by the temperature of the third zone and varied in the experiments in the range of 0.08–0.3 g/min (T_3 = 300–350°C). The temperature of aluminum (T_2) varied in the range of 450–500°C. The temperature of the pyrolysis zone (T_1) was 950–1050°C. The process was carried out under atmospheric pressure.

The electron-microscopic investigation of the prepared films was performed using a JEOL-840A scanning electron microscope. The prepared samples were also studied by X-ray diffractometry (Θ-2Θ) in the configuration of a double-crystal diffractometer on a BRUKER D8 Discover laboratory source of X-ray

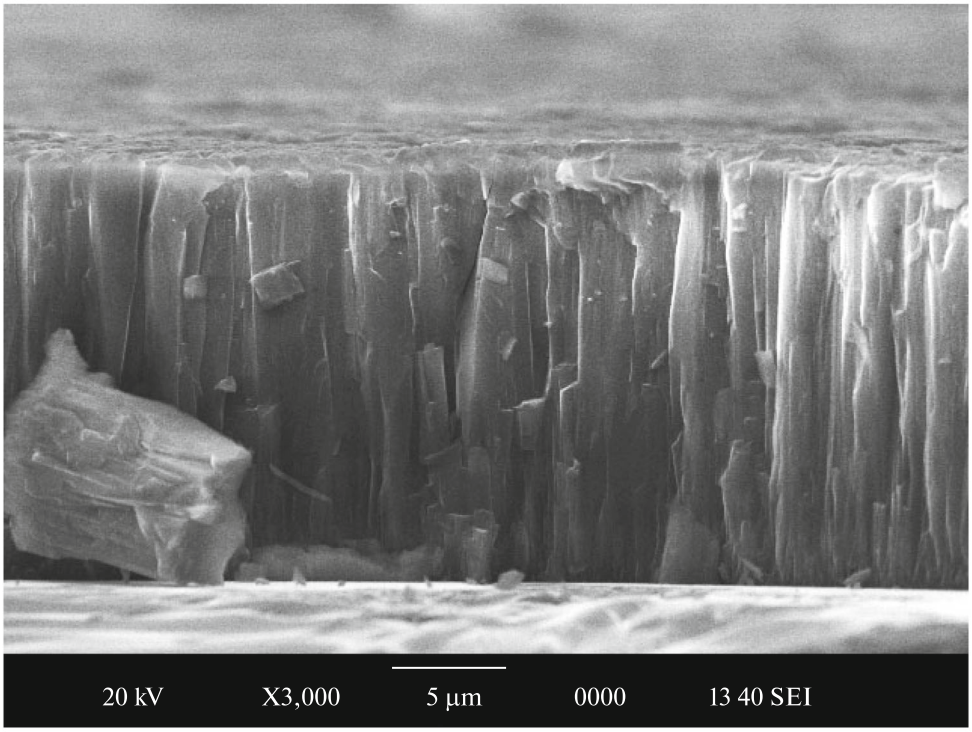

Fig. 1. REM image of the cross-section chip of polycrystalline AlN film on a silica substrate.

radiation equipped with a rotating copper anode (CuK_{α_1}, radiation, $\lambda = 1.54$ Å, $U = 40$ kV, and $I = 110$ mA). Raman spectra of the samples were studied using a Sentera Raman microscope made by Bruker upon excitation with a solid-state laser with the wavelength of 532 nm.

RESULTS AND DISCUSSION

It was mentioned that the chemical vapor deposition used in this work is a variant of the chloride-hydride method. However, in contrast to the conventional chloride-hydride method, in which toxic and chemically aggressive ammonia and hydrogen chloride are used as precursors [10], we replace it by nontoxic inexpensive salt represented by ammonium chloride, which is easy to prepared and retain in a high-purity state. It is known that NH_4Cl easily sublimes upon heating to decompose in the gas phase into ammonia and hydrogen chloride. On the whole, the following chemical reactions occur in the suggested deposition process of AlN in various zones of the reactor:

$$NH_4Cl = NH_3 + HCl, \quad (1)$$

$$Al + 3NH_3 + 3HCl = AlCl_3NH_3 + 2NH_3 + 3/2H_2, \quad (2)$$

$$AlCl_3NH_3 = AlN + 3HCl. \quad (3)$$

Varying the temperature of the first zone, one can control the rate of evaporation of ammonium chloride, which affects not only the rate of the film growth but also its morphology. It was determined that sufficiently large edged AlN crystals are formed in the reaction mixture at a large excess of ammonium chloride, which do not have a strict orientation with respect to the substrate. With a decrease in the concentration of excess ammonium chloride, the formation of a continuous polycrystalline film of aluminum nitride is observed, which consists of the interlocked columnar crystals oriented along the *c* crystallographic axis perpendicular to the substrate surface. This difference of the film morphology was also observed under identical conditions of the consumption of reagents for the substrates that are located at the start and the end of the high-temperature zone of growth. The studies suggested the optimal conditions for the growth of textured AlN films. An example of such a film is given in Fig. 1.

In order to confirm the good texture of the prepared films, they were investigated using Raman scattering (RS) and X-ray phase analysis. It was shown in [11] that the texture of AlN films can be evaluated by the intensity ratio of the main peaks in the Raman spectrum, which correspond to the E_2(high) and A_1(TO) vibrational modes. When excited by the laser orthogonal to the surface in the films with a good texture, the peak of the A_1(TO) is almost absent. Indeed, as follows from Fig. 2 (curve *1*), the A_1(TO) peak has a negligible intensity as compared to the E_2(high) peak in the Raman spectrum of the prepared film, which

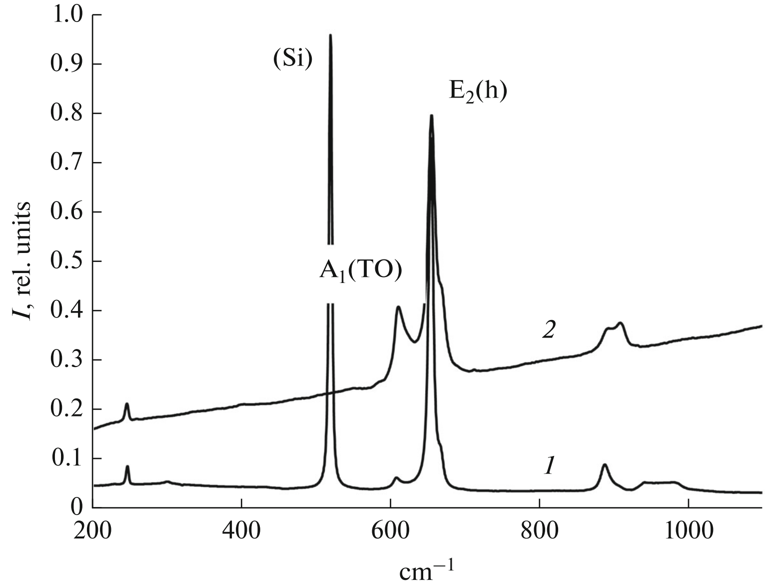

Fig. 2. Raman spectra of aluminum nitride. (*1*) polycrystalline film prepared in this work by the CVD method and (*2*) ceramics prepared by sintering the powder.

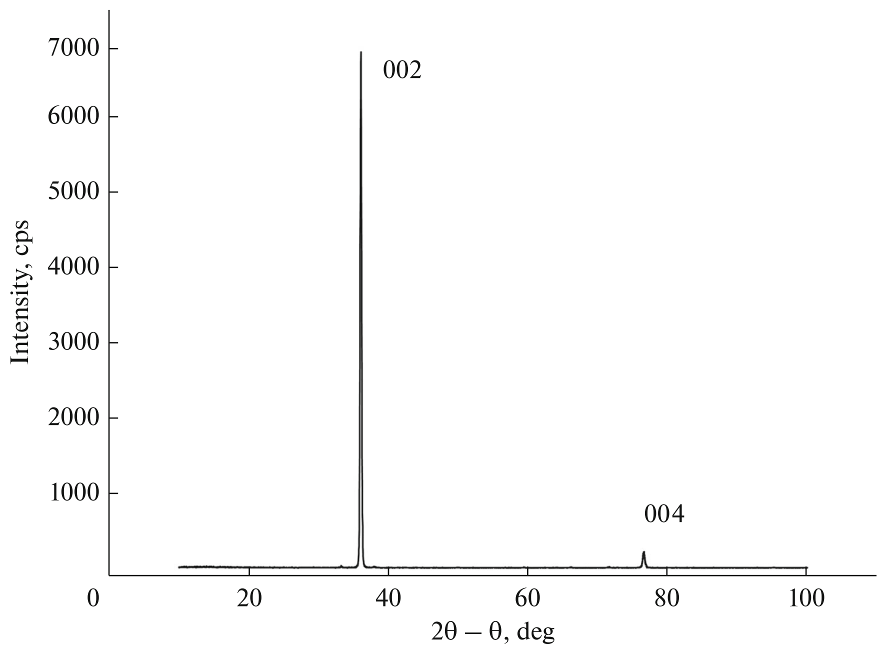

Fig. 3. Diffractogram of polycrystalline aluminum nitride film.

confirms the presence of a good texture. For comparison, the spectrum of the ceramics made from AlN is given, where there is no predominant orientation of the crystallites. It is seen that the relative intensity of the A_1(TO) peak is sufficiently high in the spectrum of ceramics (Fig. 2, curve *2*).

The good texture of the prepared films is also proved by the X-ray diffractometry. There are only the reflexes, which correspond to the planar distances (002) and (004) of the crystal lattice of AlN, on the diffractogram of the obtained film (Fig. 3). The absence of reflexes, which correspond to other planar distances, states the orientation of film-forming columnar crystals along the *c* crystallographic axis perpendicular to the substrate surface.

CONCLUSIONS

The study has shown that textured aluminum nitride films of a high crystal quality can be prepared by a relatively simple method using the inexpensive, nontoxic, and nonaggressive initial reagents represented by metallic aluminum and ammonium chloride.

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