Investigation of the structure of an aluminum nitride film for a Bragg reflector obtained by magnetron sputtering

L Baranova¹,², B Baysova¹,², V Strunin¹,²

¹Dostoevsky Omsk State University, Omsk, Russian Federation
²Institute of Radiophysics and Physical Electronics OSC SB RAS, Omsk, Russian Federation

baranova@omsu.ru

Abstract. The phase composition of the aluminum nitride film obtained through magnetron sputtering was determined with the help of X-ray phase analysis. The analysis revealed the AlN, Al and V phases deposited during the synthesis of the film. The structural parameters of the primitive unit cell of the AlN and Al phases were determined. The effect of texturing the resulting film was detected.

1. Introduction.

Microwave resonators with a Bragg reflector on bulk acoustic waves (BAW) are widely used in modern electronics due to their good reproducibility [1]. At the same time, piezoelectric aluminum nitride films can be used as a resonant element in thin film resonators [2]. Since the efficiency of a Bragg reflector directly depends on the structure, phase composition and the surface morphology of thin films [3], it is important to study the characteristics of thin film coatings.

The aim of the paper is to investigate the phase composition of aluminum nitride thin films obtained through magnetron sputtering.

2. The experimental procedure.

The phase composition of aluminum nitride films was studied with the help of X-ray phase analysis done on the Bruker D8 Advance device. In this case, the characteristic radiation of the Cu-Kα X-ray tube, with a wavelength of 1.541 Å, was used. Bragg-Brentano geometry for reflection was used to photograph the samples of thin films (≈ 1 microns), with the range of 2θ 25-75 ° angles. Scanning was performed symmetrically (θ - 2θ) scan), the angle between the sample surface and the X-ray tube was equal to the same angle between the surface and the detector. The magnitude of the step 2θ in the angle was 0.02 °, and the accumulation time was 3s at each point.

A Goebel mirror was additionally used to reduce the effect of defocusing caused by the height of the sample, the beam spread and the influence of possible inhomogeneities. The use of this device makes it possible to form a quasi-monochromatic parallel beam of primary X-ray radiation. The X-ray diffractogram for the film substance was obtained by subtracting the diffractogram of the pure substrate from the "film+substrate" diffractogram. The phase analysis of the film, as well as the...
calculation of the parameters of the primitive unit cell of the phases, was carried out according to the positions of individual peaks. The parameters and their allowances were calculated with the help of POLYCRYSTAL software package.

3. Results and discussion.
X-ray phase method was used to analyze the composition of the ceramized glass substrate, as well as the phase composition of the substrate with the film. According to the analysis data, such phases as TiO$_2$ with rutile structure (SGM P4$_2$/mmn), SiO$_2$ with a quartz structure with various sand gravel mixes/SGM (RP $1_2$ 21 and P6 $2_2$ 22) and with a cristobalite structure (Fd3m SGM) are present in the composition of a clean substrate without a deposited substance (see Fig. 1.). The formation of complex oxides (CaSi$_2$O$_5$ or Ca$_2$Ti$_2$O$_6$) was also recorded.

![Figure 1. X-ray pattern of a clean substrate (ceramized glass).](image)

An X-ray pattern of a film with a substrate (see Fig. 2.) detected TiO$_2$ phases with rutile structure, SiO$_2$ in quartz structure (SGM P3$_2$121), CaSi$_2$O$_5$, Ca$_2$Ti$_2$O$_6$.

![Figure 2. X-ray of the substrate with the AlN film.](image)

However, there were no reflectances characteristic of quartz with SGM P6$_2$22, as well as peaks for cristobalite. In particular, a noticeable difference in the diffraction pattern is the absence of a strong reflectance attributed to the 101 quartz reflectance with SGM P6$_2$22. These differences may clearly indicate the heterogeneity of the used ceramized glass substrate, which may negatively affect the results of X-ray phase analysis. Small peaks, which can be attributed to the AlN and Al phases, are also noticeable.
When the difference X-ray pattern was obtained (see Fig. 3.), the regions with negative intensity were observed in the diffraction profile. This is explained by the effect of the part of the X-ray radiation absorbed by the film and depends on the thickness of the applied film. In order to eliminate this effect, a correction for intensity values was introduced for the final X-ray pattern along the entire profile with focus on the SEM and EDX analysis data. These data show that the ratio of the Al fraction to the N fraction was 2:1, that is, it was assumed that the sample contained 67% Al and 33% N. It is worth noting that despite the correction, there was an obvious heterogeneity in the phase composition of the conditionally pure substrate and the substrate with the film. Due to this, the range of the diffractogram under study was reduced to exclude the problem zone with missing quartz peaks (Fig. 3 shows the range under study as a rectangular region).

![Figure 3](image.png)

**Figure 3.** The difference x-ray pattern obtained by subtracting the diffractogram of the substrate from the diffractogram of the substrate with the film.

A number of clearly distinguished reflectances were also detected on the resulting diffractogram (see Fig. 4.). On the basis of the assumptions about the possible composition, a coincidence in the positions of a number of peaks for the hexagonal AlN phase was found. A mismatch of intensities for a number of this phase reflectances is noted. In particular, the peaks with hk0 indices (100 and 110) were rare, and the intensity of the 002 reflectance was significantly increased. This phenomenon may indicate the presence of texture in the sample, that is, the preferred orientation of polycrystallites of the substance. Due to the latter, the corresponding crystallographic planes are found in the reflecting position (002 in our case).

Also, in addition to the hexagonal AlN phase, a significant amount of metallic Al was found in the sample. This explains the data of the EDX analysis, which showed a deviation from the stoichiometric ratio of Al and N towards an excess of Al. In addition to the AlN and Al phases, weak reflectances, which can be attributed to V and V$_2$O$_5$, were also detected. All these data correlate quite well with the purpose of the synthesis method planned to be used for obtaining a film with V, Al and hexagonal AlN phases. The formation of vanadium oxide impurity can be due to the oxidation of metallic vanadium in the air.

The primitive unit cell parameters were calculated for the AlN and Al phases. In the case of hexagonal AlN, the parameters have the following values: $a = 3.1191 \pm 0.0096$ Å, $c = 4.977 \pm 0.0098$ Å, which is in good agreement with the reference data ($a = 3.1114$ Å, $c = 4.9792$ Å)[4]. For Al, the cell parameter was a lower value ($a = 4.0352 \pm 0.0027$ Å) compared to reference data ($a = 4.0494$ Å) [4]. In this case, apparently, there is an error in determining the position of aluminum peaks since this phase has a conductometric calibrator with a maximum atomic packing density of 74%. As a result, the parameter cannot be much less than the standard value.
Figure 4. The difference AlN X-ray pattern normalized with the film thickness taken into account (the indices are given for the hexagonal modification).

The studies of aluminum nitride thin films through X-ray phase analysis proved the heterogeneity of the phase composition of the used substrates and the increased quantity of aluminum in the studied films. The X-ray image obtained by subtracting the curves of the "substrate" and "film+substrate" diffractograms revealed the phases AlN, Al and V deposited during the synthesis of the film. The structural parameters of the primitive unit cell of the AlN and Al phases correspond to the reference data in an acceptable way. The effect of texturing of the resulting film was detected. It manifested in a decrease in the intensity of 100 and 110 reflectations and a sharp increase in the 002 reflectation intensity.

Thus, the study shows the possibility of obtaining films of the required quality by varying the process conditions of their formation.

References:

[1] Sorokin B.P., Kvashnin G.M., Novoselov A.S., Bormashov V.S., Golovanov A.V., Burkov S.I., Blank V.D. Excitation of hypersonic acoustic waves in diamond-based piezoelectric layered structure on the microwave frequencies up to 20 GHz // Ultrasonics. 2017. V. 78. P. 162–165.

[2] Development and research of composite acoustic resonators with the "Al/(Al, Sc)/Mo/Diamond" structure with high finesse of the microwave / B.P. Sorokin, A.S. Novoselov, G.M. Kvashnin, N.V. Luparev, N.O. Asafyev, A.B. Shipilov, V.V. Aksenekov // Physical acoustics. 2019. Vol. 65. No. 3. Pp. 325-331.

[3] Zhang Y., Wang Z., Cheeke J.D.N. Resonant spectrum method to characterize piezoelectric films in composite resonators // IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 2003. V. 50. P. 321–333.

[4] Khramov A.S., Lukyanov I.V. X-ray diffraction analysis of polycrystals. Part IV. Study guide for the students of the Institute of Physics. Kazan: K(P)FU, 2010 - 76 p.

The study was carried out within the state assignment of Omsk Scientific Center of SB RAS (the project state registration number 121121700062-3)
The authors express their gratitude to the staff of Analytical and Technological Innovation Center "High Technologies and New Materials" (ATIC HTNM) of NSU for the assistance in carrying out the measurements.