OBTAINING THIN FILMS OF ALN BY ATOMIC LAYER DEPOSITION USING NH_3 OR N_2H_4 AS PRECURSORS.

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Abstract: In this work we used atomic layer deposition (ALD) method to obtain thin films of AlN using tris(diethylamido)aluminum (III) (TDEAA) with hydrazine (N_2H_4) or ammonia (NH_3) as precursors. Elemental analysis of the film deposited by ALD TDEAA /N2H4 at 200 °C showed the presence of carbon impurities ~ 1.4 at%, oxygen ~ 3.2 at.% and hydrogen 22.6 at.%. The atomic concentration ratio of N/Al was ~ 1.3. The residual impurities content with N_2H_4 was lower than with NH_3. In general, it has been confirmed that hydrazine has a more preferable surface thermochemistry than ammonia.

Keywords: atomic layer deposition, aluminum nitride, wide band-gap, thin films fabrication, semiconucting materials, hydrazine, ammonia, tris(diethylamido)aluminum.

1 INTRODUCTION

Aluminum nitride is a wide band gap semi-conducting material (~ 6.2 eV) with high values of thermal conductivity (2.85 W/cm · K at 300K), melting point (2750 ° C), electrical resistivity (10^{13} Ω · cm), refractive index (~2.0), but with a low adsorption coefficient ($<10^{-3}$) [1]. Such properties make AlN a promising material for a wide range of applications, e.g. power engineering, microelectronics and optoelectronics. AlN thin films have been successfully used for passivation of GaN, GaAs, SiC, InGaAs, and H-C (diamond) devices [2], and also for the excitation of surface acoustic waves [3]. AlN epitaxial layers are also used as buffer layers for the growth of qualitative GaN films and nanowires by molecular beam epitaxy (MBE) [4].

Until recently, AlN thin films have been mainly prepared by chemical vapor deposition (CVD) [5], physical vapor deposition (PVD) [3], molecular beam epitaxy [4] etc. Compared with them the ALD method has a number of advantages: relatively low deposition temperatures; the ability to control the film thickness at the atomic level; the possibility of highly conformal coating of micro/nano structures, as well as nanoparticles. In the ALD method, the growth of films occurs as a result of repeated surface reactions that are carried out far from thermodynamic equilibrium. The first work on the thermal atomic layer deposition of AlN was carried out using ammonia (NH_3) as a nitrogen precursor in combination with trimethylaluminum (TMA) or aluminum chloride ($AlCl_3$), requiring high deposition temperatures of 325-500 ° C. At the same time, films obtained on the basis of TMA/NH3 usually contain carbon impurities from 4 to 7 at% and a significant amount of hydrogen [8]. This is due to thermal decomposition of TMA and a low reactivity of ammonia [7]. To fully realize the practical applications of the third group elements nitrides, it is necessary to enable the growth of these compounds and heterostructures based on them at temperatures below 300 °C. In this regard, considerable attention is paid to plasma-stimulating methods of atomic-layer deposition of films (PS-ALD). Previously, the possibility of obtaining AlN films by the PS-ALD method from various precursors was demonstrated: $AlCl_3$ and NH_3/H_2 [16]; gas mixture $NH_3/H_2/Ar$ [9] (at 350 ° C); TMA and NH3 [10] or N_2/H_2 [34] (100-500 ° C). The use of plasma extends the possibilities in the choice of material properties, substrate temperature, precursors and processing condi-

tions, but it has drawbacks - a decrease in the conformality of the film and the risk of its damage by plasma [11].

Previously, a low-temperature ALD at 200-250 ° C using tris(dimethylamido)aluminum (Al2(N $(CH_3)_2)_6$) and NH_3 was carried out by the authors [12]. The AlN films obtained by them contained impurities of carbon and oxygen less than 1 at.%. However, the deposition conditions and the optimization process, etc. are not described in detail in Ref. [12]. A more detailed description of the conditions of the ALD AlN films using tris(dimethylamido)aluminum (TDMAA) and NH_3, within temperatures from 180 to 400 °C, was later presented in [13]. Most of the above-mentioned researchers used NH3 as the precursor of nitrogen when depositing AlN films, but N_2H_4 has a more advantageous thermochemistry for the growth of metal nitrides. The high reactivity of N_2H_4 is due to the relatively weak N-N bond in N_2H_4 compared to the N-H bond in NH_3 bond [14].

The present work is devoted to the development of optimal regimes for AlN ALD using tris(diethylamido)aluminum at temperatures below 300 °C and without employing plasma. The structure of the TDEAA molecule is shown in Fig. 1. It should be noted, that AlN films using tris(diethylamido)aluminum, were not previously obtained by the ALD method. To successfully implement this method, a high vapor pressure and thermal stability of the organometallic precursor are necessary. Compared to TDMAA, TDEAA has a lower melting point, and possibly a higher thermal stability. According to the manufacturer's database, TDMAA melts at temperatures between 28 and 31 °C, whereas TDEAA melts at between 82 and 84 ° C. It has also been indicated earlier that a similar CVD precursor of tetrakis(diethylamido)titanium, used to precipitate titanium nitride, is more thermally stable than tetrakis(dimethylamido)titanium [15].

Figure 2 shows a simplified diagram of a single ALD cycle of the proposed AlN deposition mechanism consisting of surface reactions of TDEAA and NH_3 or N_2H_4.

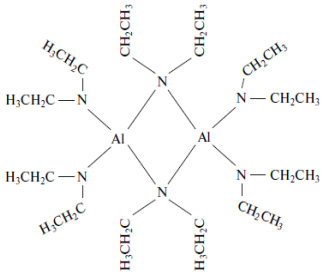

Figure 1: Tris(diethylamido)aluminum (TDEAA)

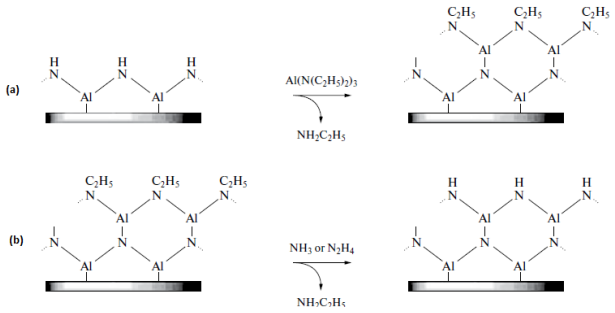

Figure 2: The proposed scheme for the precipitation of AlN ALD using TDEAA and NH_3 or N_2H_4.

2 EXPERIMENTAL DATA

The results of the x-ray photoelectron spectroscopy (XPS) analysis of the nitride film with a thickness of 300 Å, obtained by ALD TDEAA/N_2H_4 at 200 °C, are given in Fig. 3. As can be seen, the

upper layer of the nitride contains impurities of oxygen and carbon. It is known [8] that substrates coated with aluminum nitride are oxidized in the air, forming a passivation film of aluminum oxide. Carbon on the surface of the films is deposited during transferring of the sample from the ALD reactor to the XPS chamber. After etching the surface of the film with argon ions, the oxygen and carbon contents are significantly reduced. The oxygen and carbon contents in the film are approximately 3.2 at.%, and 1.4 at.% respectively. The presence of oxygen in the bulk of the film is explained by the presence of oxygen as an impurity in the dosed N_2H_4, in addition, it is known that hydrazine is hygroscopic [16]. The presence of carbon in the bulk of the film is an indicator of the non-ideal nature of the processes occurring on the surface. The presence of a carbon impurity can affect the dielectric properties of the AlN film [17]. The absence of significant carbon impurities in the films obtained by us indicates that reaction B (Fig. 2), with N_2H_4 dosage, practically passes to completion.

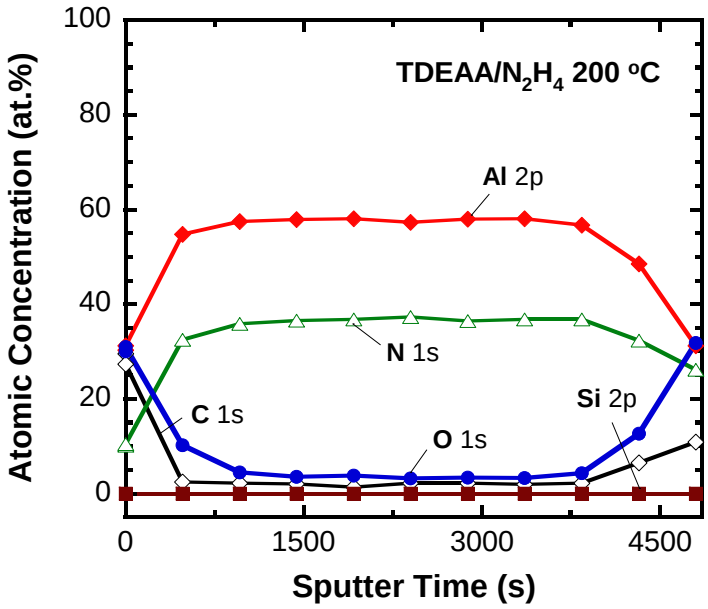

Figure 3: XPS data on the atoms distribution in the bulk of the ALD AlN film obtained using hydrazine at 200 °C.

Hydrogen is one of the most frequently encountered impurities in AlN films grown by thermal and plasma-stimulated ALD methods. In the present work, the content of hydrogen atoms in the films was determined by the forward recoil elastic spectroscopy (FReS). Figure 4 shows the FReS spectra of ALD AlN films 980 and 550 Å thick, obtained at 200 °C using N_2H_4 and NH_3. Analysis of the samples indicates that hydrogen is present in the films in 22.7 at.% and 26 at.% for systems with N_2H_4 and NH_3 respectively. This indicates that the reaction of TDEAA with surface ($-NH_x$) groups, (reaction A Figure 2), may not be complete, which may be the reason of the hydrogen impurities presence.

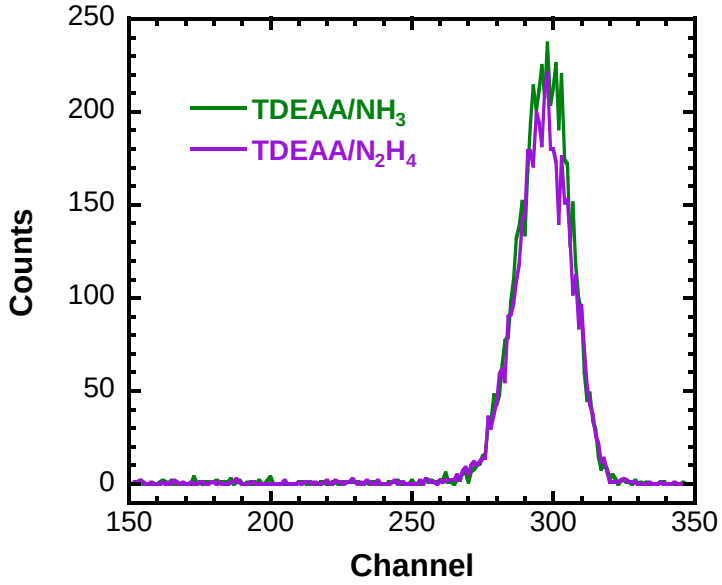

Figure 3: FReS Spectra for two AlN samples deposited using ammonia and hydrazine at 200 °C.

The values of the hydrogen concentration in the films obtained by us are slightly lower than in the films grown at 200 °C using TDMAA/NH3 by the ALD method (30 at.%) [13] and CVD (11-31 at.%) [5, 6]. Films obtained by ALO ALN at 350 and 500 °C using NH_3 and TMA or $AlCl_3$ contain hydrogen at about 9-15 and 9 at.%, respectively [8]. The annealing of films obtained in the present study was not carried out. Even with high hydrogen content, the films obtained in this work can find potential applications in microelectronics.

3 CONCLUSION

Results of this work suggest that an exemplary structure of AlNH with only some insignificant impurities of oxygen and carbon can be obtained by the ALD method at relatively low temperatures when using N_2H_4 or NH_3 as precursors. At the same time, hydrazine has a more advantageous surface reactivity with TDEAA, which increases the density of the films at equal conditions. By the level of their density and roughness the obtained films are comparable and in some cases superior to the samples of AlN films obtained by the thermal and plasma-stimulated ALD. The amount of oxygen in films obtained using TDEAA and N_2H_4 can be reduced using hydrazine with a purity above 98%. It should be also mentioned that obtained AlN films contained relatively high level of hydrogen impurities, which is a problem for many ALD AlN systems. However, it can be solved by high-temperature annealing of the samples which allows preserving an exceptional homogeneity of the layer, as is the case in thermal ALD. The precursors and deposition parameters of AlN thin films proposed here can be considered as an alternative to traditional plasma-stimulated and high temperature ALD techniques.

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