Formation of nanoscale structures in thin films deposited by reactive magnetron sputtering of binary metal targets in Ar+O$_2$+N$_2$ gas mixture

D Bernt$^1$, V Ponomarenko$^1$, S Leshchev$^2$ and A Pisarev$^2$

$^1$ Pilkington Glass, 1 Stekolnaya Str, Zhukovo village Chulkovsky s/o Ramensky District, 140125 Moscow region, Russia
$^2$ National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, 115409 Moscow, Russia

E-mail: Dmitriy.Bernt@spglass.ru

Abstract. Bi-metal targets of ZnSn and SiAl were sputtered in Ar+O$_2$+N$_2$ gas mixtures at various N$_2$/O$_2$ ratios, and the deposited films were investigated by AFM and XPS. No nitrogen was detected in the films even at the highest nitrogen partial pressure in the gas, and the films were oxides. The concentration of the doping metal component in the deposited film increases with the increase of nitrogen partial pressure in the working gas. These experimental observations were supported by numerical calculations of the sputter-deposition process using a SRIM/SIMTRA+RSD software. It was shown that added nitrogen promotes sputtering of doping metal components of the targets, and the concentration of oxygen remains high enough to substitute the less active nitrogen in the growing film. The films consisted of nanograins with the average diameter, which decreased from 18 nm to 3 nm with increase of nitrogen content in the working gas. This effect was explained by the mechanism of abnormal grain growth: the film consisted of grains of oxides of two metals with different concentrations. The doping metal forms very fine nanograins of oxides, which suppress the growth of oxides of the main metal. With increase of nitrogen in the working gas mixture, the sputtering rate of doping metals from the cathodes and their respective concentration in the growing films increases, so the average diameter of oxide grains forming the coating decreases.

1. Introduction

In recent years, oxinitride thin films have attracted much attention, because of their versatile properties important for optics, photonics, microelectronics, oleophobic, catalytic, cutting tools, battery cells, and other applications [1-5]. Oxides and nitrides often have opposite behaviors with respect to film properties, therefore oxinitrided sometimes offer a compromise between the extreme behaviors, and controlled introduction of nitrogen to oxides leads to a good control of designed properties [6-13].

Functional properties of oxides, nitrides, and oxinitrides are connected with their structure, which, in turn, depends on many factors. Films can be amorphous like in [10] and crystalline like in [11]. The grain sizes may become less with the increase of the film thickness [12]. Films deposited at room temperature [6, 10, 11] were amorphous but became crystalline at annealing with the lattice parameters dependent on the nitrogen content. Phenomenological study [3-5, 13] of oxinitride films deposited by
magnetron sputtering demonstrated dependence of the film properties on O₂/N₂ flow rate in the reaction chamber.

Among the properties of interest for many applications, oleophobicity - which in general states for the surface repelency of viscous liquids - must be mentioned. It was demonstrated in [13, 14] that addition of N₂ to O₂ during magnetron sputtering of binary metal Zn-Sn and Si-Al targets leads to up to 45% increase of the oleophobicity of deposited thin films according to the droplet spread diameter and contact angle measurements tests. Also it was observed that nanoscale grains become smaller due to N₂ addition, and this can result in the increase of the surface oleophobicity [15].

The aim of this work is to study features and mechanisms of formation of such films and elucidate the role that nitrogen plays in deposition of films sputtered from bi-metallic targets in Ar+O₂+N₂ gas mixture.

2. Experimental
Deposition of films was performed in an industrial line VonArdenne GC330H for architectural glass coating. A dual rotating cylindrical magnetron system, driven by a TRUMPF Hüttinger TruPlasma power supply, installed in the line chamber was used for sputtering. It operated in pulsed DC mode at the frequency of 34 kHz and the power limit of 70±4 kW. The sputter targets were made of binary ZnSn and SiAl alloys. Substrates for test depositions were made of quartz microscope glass with the thickness of 1mm and dimensions of 75×25 mm. They were cleaned in deionized water and then dried with compressed dry air. No heating was applied towards the substrates during the deposition.

Three series of reactive sputter depositions were performed. The first and the second series were performed with ZnSn target with two different alloying concentrations (10wt% Sn and 50wt% Sn respectively) In the third series SiAl (10wt% Al) sputtering target was used. The minimal purity for the alloys used was 99.7% with the alloy concentration stability of ±2 wt.%. Sputtering was performed in a mixed gas atmosphere Ar+O₂+N₂. The gas supply was controlled by MKS mass flow controllers. Oxygen and argon flows were set to operate magnetrons in the transition mode of the cathode poisoning hysteresis, which resulted in O₂ flow of approximately 900 sccm through the whole set of experiments. The total resulting gas pressure in the chamber was maintained at the level of approximately 3.5×10⁻³ mbar. Nitrogen flow varied from 0 to 800 sccm with the step of 100 sccm within every series. Deposition experiments were performed in the so called transition reactive sputtering mode, which is the intermediate operating regime between the metallic and fully poisoned modes on the reactive sputtering hysteresis. The operation regime was controlled through optical emission of exited atoms of the gas and metal in plasma of the magnetron discharge with a feed-back regulation of the gas flow rates.

The thicknesses of the deposited coatings were in the range of 120-135 nm. Their thicknesses were established and then maintained at the given range via indirect control based on the spectrophotometric ex-situ measurement in the range of wavelengths between 350 and 1300 nm. Spectra were obtained in transmission and film-side reflection from the samples.

Elemental analysis of coatings was performed using X-ray Photoelectron Spectrometer Kratos XSAM-800. Exitation was made using the AlKα (1486.6 eV) radiation. Bruker FastScan AFM with a silicon nitride cantilever (silicon tip ~1nm in diameter) operated in peak force taping mode was used to determine the topography of the coatings.

3. Results
AFM analyses demonstrates that deposited films consist of very fine rounded grains (approximately 5-20 nm in diameter) in all experiments (Fig. 1-a). Nitrogen addition in the gas always leads to decrease of the grain size and respective smoothening of the film surface. The same effect was also observed previously [14].

The average grain diameter of the coatings surface as a function of the nitrogen flow demonstrates prominent decrease of the grain diameters at the nitrogen flow rate of about 350-400 sccm, which is approximately a half of the oxygen flow rate used. At higher values of the nitrogen addition, the average
grain diameter decreases much slowly remaining at the level of the resolution limit of the AFM tip (Fig. 1-b).

**Figure 1.** AFM surface morphology analysis: a) height and peak force error images of the film surface deposited by sputtering of the Zn+10wt.%Sn target at the nitrogen gas flow of 350 sccm; (b) dependence of the average diameter of surface grains $G$ on the nitrogen flow rate for three targets used for sputtering.

Fig. 2 shows XPS spectra obtained from the virgin film surface and from the film sputtered by Ar$^+$ ion beam just before XPS measurements. These measurements demonstrate no nitrogen both on the surface of the film and in its bulk. No nitrogen was found for all films independent on the sputter target composition and nitrogen-to-oxygen flow ratios used. One must note that the peak of Sn in the film is higher if the flux of N$_2$ is higher. This is well seen for two ultimate cases represented in Fig. 2: no nitrogen and 800 sccm of nitrogen.

**Figure 2.** Example of the results of XPS analysis for ZnSn (50wt% Sn) coatings. Frame (a) XPS from as deposited film, frame (b) XPS after etching by Ar$^+$ ions for 6 min. Bottom spectra are for 0 sccm of N$_2$ flow, top spectra are for 800 sccm of N$_2$ flow.

4. **Discussion**

The feature of the films deposited by sputtering of bimetal targets is nanoscale dimensions of their grains. One may suggest that such grains grow according to the so-called abnormal grain growth process, which is also referred to as exaggerated or secondary recrystallization grain growth mechanism. This mechanism suggests that atoms of the more reactive elements in relation to oxygen (like doping component or an impurity) that are deposited on the substrate form fine oxide grains. Those define the formation of the oxide grains of the main element upon them, and as a result restrict the dimensions of
the final granular structure [16]. The abnormal grain growth process is encountered in metallic or ceramic systems exhibiting secondary phase inclusions above a certain threshold concentration. It is quite well-known especially for the ceramic materials, as this phenomenon can result in improved fracture toughness through the impedance of crack propagation [17].

In our case, atoms of the doping components on the cathode and on the substrate are more active in regard to oxidation, therefore they form oxides more actively than atoms of the main metal components. Due to high oxidation rate, the concentration of oxides of the active component is very high, while the dimensions of oxide grains of these components is respectively small. Oxidation of the main metal component takes place slower, and the respective oxide grains grow in the matrix of fine grains of the more active component. Therefore the dimensions of the oxide grains of the less active component are restricted by fine grains of the more active component. The higher is the concentration of the active component, the higher are the concentration and smaller sizes of its oxide grains, and respectively the smaller are dimensions of oxide grains of the less active component.

The resulting average grains size of the multielemental layer, which grow due to the abnormal grain growth process, can be described with the Clarke equation (1) [18]:

\[ \delta = \frac{1}{3} \left( \frac{x_i - x_i^0}{x_i^L} \right) G \]

where \( x_i \) is the concentration of the more active component introduced in the system, \( x_i^0 \) is the solubility limit, \( x_i^L \) is the equilibrium concentration of the active component in the liquid phase, \( \delta \) is the thickness of the forming film and \( G \) is an average grains diameter. It is assumed that the individual elements are distributed uniformly within the growing coating layer and all grains are all spherical [19].

Fluxes of metal atoms depositing on the substrate due to the reactive sputtering of the bimetal can be quantitatively simulated by SRIM/SIMTRA+RSD software package [20]. Time evolution of the target and film compositions is calculated. Modeling is performed taking into account configuration of the experimental system and parameters of the experiment. Non uniform ion flux on the cathode, redeposition and re-sputtering, as well as the chemical reactions on the cathode and on the substrate are taken into account in the code.

Computer simulation verified the experimental observation that in conditions of this work no nitrides are formed in films deposited on the substrate, and only oxides are formed. This conclusion was true for all bimetal targets and nitrogen flow rates used in the experiments. This is apparently connected with a higher reactivity of oxygen which tends to substitute nitrogen both on the sputtered target and in the growing film. Formation of oxinitrides and nitrides during the reactive sputtering \( \text{O}_2^+ + \text{N}_2 \) mixture is possible only in the case of very high nitrogen partial content.

A support of this conclusion can be obtained from auxiliary experiments on observation of optical emission of plasma components in the transition reactive sputtering state, which was used in experiments. As it was shown in [21], two extreme regimes are realized during sputtering of Ti in \( \text{O}_2^+ + \text{N}_2 \) mixture depending on the balance between \( \text{O}_2 \) and \( \text{N}_2 \). In the case of relatively low concentration of nitrogen, only oxides are formed on the substrate, and this mode is called “oxide” mode. In the case the concentration of nitrogen is high, oxinitrides are formed on the substrate, and this mode is called “nitrile” mode. If during operation the regime shifts from the metallic state to the “oxide” mode of transition state, the characteristic emission of oxygen increases, while the characteristic emission of the metallic components decreases. If during operation the regime shifts to the “nitrile” mode, the characteristic emission of nitrogen increases, while the characteristic emission of the metallic components changes either moderately or negligibly.

Just this behavior was observed in our experiments demonstrated in Fig.3. One can see that even at the highest nitrogen flow rate used in our experiments (800 sccm in Fig.3a), the sputter deposition is in the “oxide” mode, and only if the nitrogen flow rate is 10-20 times higher than the oxygen flow rate (4500 sccm in Fig.3b) the deposition is in the “nitrogen” mode. This explains why no nitrogen was observed in our experiments even at the highest nitrogen flow rates.
The experimental regimes were simulated numerically, and the result agrees with the experiment. For example, observation of nitride components in the film was predicted to be possible at the value of N$_2$ to O$_2$ ratio of 16:1 for Si+10wt% Al target.

![Figure 3](image)

**Figure 3.** Time trends of plasma discharge optical emissions monitoring for the according elements’ characteristic emission (as noted in the trends) during process switching from metallic into the transition reactive sputtering regime at 800 sccm of N$_2$ flow (a) and 4500 sccm N$_2$ flow (b).

Experimental observation of the increase of the dopant oxide content on the substrate with the increase of nitrogen flow rate was confirmed by numerical simulations. Fig. 4-a demonstrates the increase of the concentration of the doping component with increase of the nitrogen flow rate for the three targets used in the experiment. It can be assumed based on the obtained results, that the state of the target surface poisoning achieved with the addition of a certain N2 flow energetically favors the sputtering of the doing component in regards to the main metal.

![Figure 4](image)

**Figure 4.** Dependency from the N2 introduction flow for a) – concentration of the doping component in the forming thin film; and b) – average grains diameter for the case of all target materials used.

The calculated concentrations of elements shown in Fig.4a were used to calculate the dimensions of crystallites according to formula (1). The results are shown in Fig.4b. One can see that the calculations perfectly describe the experimental data shown in Fig.1b.
5. Conclusion
Composite Zn+10wt. % Sn, Zn+50wt. % Sn, and Si+10wt. % Al targets were magnetron sputtered in the reactive O$_2$+N$_2$ gas mixture. Thin films deposited on the substrate consisted of fine round-shaped nanograin. The increase of nitrogen content in the gas mixture led to decrease in the average diameter of the grains. No nitrogen was observed in XPS for all the coatings deposited in a wide range of the O$_2$/N$_2$ ratio. It was suggested that oxygen substitutes nitrogen on the target and on the substrate due to its higher chemical activity in conditions of the experiment. Auxiliary experiments on optical emission of atoms sputtered from the target and then exited in plasma demonstrated that the process in the so-called “oxide” mode, where no nitrides are expected on the substrate. Nitrides can be expected at nitrogen flow rates an order of magnitude higher than those used in the experiments performed. Sputter-deposition process was modelled numerically by SRIM/SIMTRA+RSD software package, which demonstrated increase of the deposition rate of Sn and Al with increase of the nitrogen content in the working gas.

The calculated deposition rates were used for calculations of the grain dimensions according to the Clarke equation that describe the so-called abnormal grain growth process, and the calculated dependences of the grain dimensions against the nitrogen flow rate perfectly described experimental dependences measured by AFM.

One can conclude that the mechanism of the abnormal grain growth can be applied to description of the grain dimensions in films sputtered in O$_2$+N$_2$ gas mixture from bimetal cathodes in magnetron discharge.

Acknowledgments
The authors acknowledge Dr Yu. Lebedinski of Moscow Institute of Physics and Technology for XPS analysis, and Dr. D. Depla and the team of DRAFT group of Ghent University for access to the PVD process simulation software packages. The work was partially supported by Grant № 14.Y26.31.0008 from the Ministry of Education and Science of Russia.

References
[1] Le Dréo H, Banakh O and Keppner H 2006 Thin Solid Films 515 952
[2] Marlec F, Le Paven C and Le Gendre L 2017 Surf. and Coat. Technol. 2017 324 607
[3] Ali S, Paul B and Magnusson R 2016 Vacuum 131 1
[4] Haye E, Capon F and Barrat S 2016 Surf. and Coat. Technol. 298 39
[5] Rawal S, Chawla A and Jayagathan R 2014 Materials Sc. and Eng. 181 16
[6] Wang Y, Wang H and Zhang J 2009 Appl. Phys. Lett. 95 032905
[7] Lei P, Guo S and Zhu J 2016 Surf. Eng. 32 585
[8] Murdoch B, Ganesan R and McKenzie D 2015 Appl. Phys. Lett. 107 112903
[9] Xu L, Nishimura T and Shibayama S 2016 Appl. Phys. Express. 9 091501
[10] Haye E, Bruyère S, André E and Boulet P 2017 Journal of Alloys and Compounds 724 74
[11] Zhaozhe Y, Huarui X and Guisheng Z 2016 Applied Surface Science 368 173
[12] Le Paven C, Benzerga R and Ferri A 2017 Materials Research Bulletin 96(2) 126
[13] Bernt D, Ponomarenko V and Pisarev A 2017 Surf. and Coat. Technol. 330 211
[14] Bernt D, Ponomarenko V and Pisarev A 2016 Journal of Physics: Conference Series 748
[15] Steele A, Bayer I and Loth E 2009 NanoLetters 9(1) 501
[16] Kang S-J L 2005 Sintering: Densification, Grain Growth, and Microstructure (Amsterdam; Boston; London: Elsevier Butterworth-Heinemann)
[17] Padture N and Lawn B 1994 J. Am. Ceram. Soc. 77 2518
[18] Clarke D R 1987 J. Am. Ceram. Soc. 70(1) 15
[19] Bae I-J and Baik S 1997 J. Am. Ceram. Soc. 80(5) 1149
[20] Strijckmans K and Depla D 2014 J. Phys.: Appl. Phys. 47(23) 235302
[21] Pinaev V and Shapovalov V 2009 Vakuum. Tekhn. Tekhnol. 19 7