Advanced processes for low-temperature formation of functional metal oxide based thin films

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Abstract. The analysis the discharge processes in magnetron plasma, target sputtering processes, as well as nucleation and formation of oxide thin films during dc magnetron sputtering is carried out. Particular attention is paid to the phenomenon of instabilities of the current-voltage characteristics of magnetron plasma during the sputtering of oxide targets, the processes of structural transformations of the surface of metal oxide targets under ion bombardment impact, and the mechanisms of low-temperature magnetron deposition of metal oxide thin films. Based on the results of the analysis performed the optimal routes for improving technologies for the low-temperature formation of transparent conductive oxide thin films have been discussed.

1. Introduction

Topics related to magnetron deposition of thin-film materials for use in electronics, photonics, and other applications have been widely studied for many years [1-3]. The rapid development of information display systems, solar cells and other optoelectronic devices has led to an active search for technologies for the synthesis of indefectible (i.e., having sufficient crystallinity and smoothness) thin films at relatively low temperatures on polymer substrates, as well as to the search for new available materials for new generation devices [4,5]. This is dictated by the urgent need to develop create roll-to-roll technologies for creation of large-area flexible display systems, thin-film solar converters and protection from electromagnetic pollution [6,7].

In addition, for several decades, the issue of replacing expensive ITO (In\(_2\)O\(_3\):SnO\(_2\)) material used as transparent electrodes with some more affordable and cheaper alternative is still very relevant for researchers and developers of information display systems [8-9]. The situation is aggravated by the fact that now the display industry's needs for expensive In are becoming comparable to the volume of its annual world total production [10].

Here an overview is given of some processes aspects observed in the magnetron discharge plasma (section 2), as well as on the sputtered ceramic target surface (section 3). Then by the example of ZnO-based transparent conductive oxide (TCO) thin films, routes for improving the structure of thin films obtained by low-temperature deposition are considered (section 4). Finally, an attempt has been made to predict the development of the issue of creating new materials and technologies for functional thin films of new generation devices.

2. Current-voltage characteristics of the plasma discharge during magnetron sputtering

The parameters of the gas discharge during magnetron sputtering largely determine the dynamics of the target sputtering process and strictly set the conditions for the deposition of thin films. The processes occurring in magnetron plasma with the participation of atoms and clusters are reviewed in great detail [11]. The current-voltage characteristics of a gas discharge have already been studied in detail [12,13].
In particular, in [11] discharge instabilities were discovered and discussed. Figure 1a shows that the I–V characteristic of a glow discharge exhibits two instability regions: during the transition from a dark to a glow discharge and from a glow to an arc discharge. It should be noted that the given data refer to the conditions of the discharge proceeding at relatively high pressures in the discharge gap.

![Figure 1](image.png)

**Figure 1.** (a) – the three primary regions of a gas discharge. The straight line is a typical load line. Reproduced with permission from Depla D, Mahieu S, Greene J E 2010 Chapter 5 - Sputter Deposition Processes. In *Handbook of Deposition Technologies for Films and Coatings* (ed Martin P M) p 262. Copyright 2010 P. M. Martin. Published by Elsevier Inc. (b) – a typical I–V characteristic of an atmospheric pressure dc discharge in a pin-to-plane electrode system. Inset – view of the filamentary mode of a non-stationary pin-to-plane dc glow discharge in ambient air. Reproduced with permission from Akishev Yu, Grushin M, Kochetov I, et al. 2005 Plasma Sources Sci. Technol. 14 S18–S25. Copyright 2005 by IOP Publishing.

It is reported that at high gas pressures in the pin – plate system, a nonstationary discharge is formed in the region of a negative corona discharge [14]. The corresponding I–V characteristic of a discharge occurring at atmospheric pressure is shown in figure 2. It is clearly shown here that the discharge instability is observed in the region of the transition of an anomalous glow discharge into an arc discharge.

In turn, the study of the I–V characteristic of a glow discharge arising between parallel flat electrodes about 11 cm in diameter in an atmosphere of N\textsubscript{2}:O\textsubscript{2} = 8:2 at a pressure in the chamber of about 10 Torr and a discharge current of about 100 A showed that the I–V characteristic of the discharge corresponds to the transition of a glow discharge into arc one [15].

In 1998 for the first time Abduev and Magomedov reported about the observation of stable current oscillations with a frequency of about 10 kHz during dc magnetron sputtering of a ZnO ceramic target [16]. They related the observed process to the sticky instability of oxygen, which leads to Trichel oscillations in a magnetron discharge in an oxygen-containing medium [17].

We believe that correct interpretations of the observed results are extremely important for practical use in the development of new modes of deposition of thin films.

The oscillation phenomenon during magnetron sputtering of ceramic ZnO targets suggests that this process is observed at the transition from an anomalous glow discharge to an electric arc discharge. The process starts only in a very narrow pressure range (about 4×10\textsuperscript{-4} Torr) when using an electrical supply circuit that forms an oscillatory circuit. An increase in the surface temperature of sputtered ZnO ceramic target in the presence of an oscillatory circuit leads to the formation of oscillations caused by sticky instability only if there is a certain oxygen concentration in the anomalous glow discharge gap. The
formation of sticky instability upon magnetron sputtering in an Ar medium is caused by thermal desorption of oxygen from the surface of the sputtered ceramic target. The observed oscillations are due to hysteresis instability accompanied by alternating transitions between the metallic and dielectric modes in the target erosion zone.

3. Target erosion during its ion sputtering
To date, ion bombardment of ceramic targets during dc or rf magnetron sputtering had been studied mainly in terms of assessing the efficiency of sputtering of the target material, as well as the instability of the discharge. It is obvious that ion bombardment of the surface of oxide targets can lead to a significant change in stoichiometry in the near-surface layer of the sputtered target. And the deviation from stoichiometry can be in one direction or another, depending on the composition of the working gas. For example, with intense sputtering of an oxide target by ions of an inert gas, the deviation of stoichiometry towards oxygen deficiency in the near-surface layers of the target erosion zone can lead to various instabilities associated with the transition of a magnetron discharge from an anomalous glowing to an arc one [18]. This leads to a decrease in the quality of deposited thin films and the reproducibility of their characteristics. On the contrary, the sputtering of targets in the presence of oxygen can lead to additional oxidation of the target surface in the erosion zone. The processes of reduction and oxidation of the surface layers of the target lead to hysteresis phenomena, which also negatively affect the stability of the characteristics of the deposited thin films [9, 19].

Based on the analysis of numerous works, it can be concluded that the processes of structural restructuring and surface self-organization of target materials in the erosion zone are still insufficiently studied.

As for the case of sputtering a ZnO-based TCO target, the bombardment of its surface with inert gas ions (Ar) leads to a gradual oxygen depletion of the thin surface layer of the sputtered target, and thus thin films on the substrate begin to grow from a flow containing excess zinc [20,21]. Such conditions results in, in turn, to a significant decrease in the resistivity of the deposited thin films [20,22].

4. Growth mechanisms of ZnO-based TCO thin films by magnetron sputtering
A large number of studies have been devoted to the study of the mechanisms of ZnO-based TCO thin films growth by magnetron sputtering. An obvious general requirement for the ZnO thin films is a high structural perfection, which provides both acceptable optical transparency and high mobility of charge carriers.

A serious drawback of the microstructure of ZnO thin films deposited by magnetron sputtering under conditions far from equilibrium layers is the formation of an obvious columnar structure in them (figure 2a). The columnar structure of the ZnO films is characterized by a poor order of crystallite orientation and a developed surface relief [23]. This leads to deterioration of optical and electrical performance of ZnO TCO thin films.

We have previously shown that in order to suppress the formation of columnar structures in the zinc oxide films, there is a need to carry out the magnetron deposition of ZnO films from the reagent flow containing excess zinc over the oxygen (figure 2b) [24]. This leads to an increase in the atoms migration length on the film growth surface due to the formation of a low-melting ZnO$_{1-x}$ phase on the growth surface at temperature of about 450°C (above Zn melt temperature). However, this does not allow solving the main problem – reducing the temperature regime to 100°C for the deposition of TCO thin films with a high degree of microstructural order and an acceptable Hall carrier mobility. The problems of the dependences of the elastic modulus of steels and alloys depending on high temperatures were discussed in detail in the articles [25-30].
Figure 2. The cross-section views of ZnO TCO thin films deposited by magnetron sputtering of ceramic target (a) and by co-sputtering ceramic and Zn targets (b).

At the same time there are other ways to improve the microstructure ZnO thin films deposited by magnetron sputtering. One of these promising ways is to create conditions for reducing the level of bombardment of the growing film surface with negative oxygen ions, especially during the film nucleation stage [23,31]. As another way, we can consider the use of various ultrathin buffer sublayers providing a high degree of orientational order at the nucleation stage [32].

5. Conclusions
The review of the currently available data makes it possible to determine the following directions for improving the technologies for low-temperature deposition of TCO thin films based on ZnO:
- use of non-stoichiometric ceramic targets;
- creation of conditions to minimize the residual oxygen pressure in the working chamber;
- assisting the deposition process at the initial stage of growth with an inert gas ion beam;
- use of substrates with minimal surface relief, as well as with a special sublayer.

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