Obtaining of non-stoichiometric titanium oxide using reactive magnetron sputtering

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Abstract. A mode of obtaining of non-stoichiometric titanium oxide film in magnetron system with turbomolecular pump of low performance was found. The mode provides significantly lower volumetric flow rate of argon and reactive gas comparing with known mode. Dependencies of discharge voltage and film sputtering rate on reactive gas volumetric flow were investigated. Measurements of film obtained by the mode with low oxygen volumetric flow proved deviation of composition stoichiometry.

1. Introduction
Non-stoichiometric compounds (oxides, nitrides) of metals and semiconductors are actively used in electronics and nanotechnologies due to their special physical and chemical properties. There are research activities on light emission diodes (LEDs) creation on quantum luminescence dots that are silicon nanocrystals in a silicon nitride film of non-stoichiometric composition [1]. Thin films of transition metals oxides that change their electrical conductivity during current flow are used as an active layer of memristors [2] and memristor crossbars [3]. In addition, memristors can be made using reduced metal oxide films. Common method of obtaining such compounds is the atomic layer deposition. This method has significant lacks related to non-uniformity of elements distribution along the film thickness and inclusion of elements participating in chemical reactions during the metal oxide deposition from precursor.

The reactive magnetron sputtering method provides purity and excellent homogeneity of metal oxide films with high deposition rate and precise thickness control [1]. However, the atomic layer deposition (ALD) method is preferable for obtaining films of metal nitrides or dielectrics because it allows selection of desirable mass ratio of elements in precursor.

Control of film chemical composition is difficult during reactive magnetron sputtering. A sputtering of cathode target material on substrate occurs within inert gas presence and low flow rate of reactive gas. When flow of the gas is high enough to form a chemical compound, the target sputtering rate reducing and a stoichiometric compound is depositing onto the substrate. When the volumetric flow of the reactive gas decreases, sputtering mode remains stoichiometric. Further reducing of the gas flow leads to rapid change of the sputtering mode to deposition of target material. Observed hysteresis (figure 1) does not allow to describe sputtering process uniquely and to predict stoichiometry of a film.

An investigation of opportunity to obtain non-stoichiometric compound of titanium oxide within low flows of sputtering and reactive gases is the main aim of presented paper.
2. Stoichiometry control
S. Berg et al. [4] presented the model of reactive magnetron sputtering for the case of titanium sputtering within nitrogen atmosphere. The simulation results shows that nitrogen-titanium ratio directly depends on the reactive gas flow. This allows using reactive gas flow as state variable. The calculated data were proved during obtaining of stoichiometric TiN. This model was used primarily to increase the rate of stoichiometric compounds deposition.

B. Hoskins and D. Strukov [5] has modified Bergs model to obtain TiO\textsubscript{x} compound of desired composition. As been shown, growth of non-stoichiometric films is possible when perturbative reactive gas flow combined with comparatively small discharge power and high argon to reactive gas partial pressures ratio. The state variable was normalized to 1, where 1 corresponds to stoichiometric composition and 0 corresponds to pure target material. The normalized state variable is called the oxidation factor. The experiment carried out at pressure of 0,08 Pa and discharge power of 150 W. Target diameter was 3 inches. Custom built high vacuum sputter chamber was pumped by Cryotorr 800 with a 1000 l/s pump rate. Argon flow rate was 190 sccm and oxygen flow rate was from 0 to 16 sccm. Experimental dependence of O/Ti ratio from oxidation factor F measured by Rutherford backscattering is approximated by hyperbolic function $O/Ti = a - 1/(bF)$, where a and b are constants.

3. Experimental
Actual experiment was carried out in compact magnetron unit of NT-MDT NanoFAB-100 complex. The work volume of the vacuum chamber is 50 liters. The unit is equipped with BOC Edwards STP-H451 low-performance turbine with a 450 l/s pump rate. A volumetric flow of gases in chamber adjusting by electromagnetic valves with accuracy of 0,1 sccm. The 99,99 % pure Ti target diameter is 78 mm. The distance between sputtering cathode target and substrate is equal 100 mm in the experiment. The vacuum chamber was pumped to remaining base pressure of $5 \times 10^{-5}$ Pa before the experiment.

Sputtering experiment was carried out in pulse mode of magnetron with constant discharge power of 115 W and constant chamber pressure of 0,1 Pa. Operating pressure was induced by 12 sccm flow of 99,99 % pure argon. Experimental dependences of TiO\textsubscript{x} films growth rate on volumetric flow of O\textsubscript{2} (figure 2) and discharge voltage on volumetric flow of O\textsubscript{2} (figure 3) were obtained varying oxygen flow from 0 to 1,4 sccm.

Experimental plots (figure 2., figure 3.) show that chosen sputtering mode allows to avoid jumping behavior of sputtering curve. Nevertheless, relatively big oxygen flow and oxidation factor more than 0,5 lead to formation of hysteresis in S(Q) and especially in U(Q) curves. That circumstance leads us...
to conclusion that composition of films grown by this sputtering mode is controllable only in plot section from \( F = 0 \) to \( F = 0.5 \) or from \( Q = 0 \) sccm to \( Q = 0.7 \) sccm.

![Figure 2](image2.png)

**Figure 2.** Experimental dependence of TiOx film growth rate on volumetric flow of O\(_2\) at constant pressure and discharge power.

![Figure 3](image3.png)

**Figure 3.** Experimental dependence of discharge voltage on volumetric flow of O\(_2\) at constant pressure and discharge power. Error bars show range of voltage varying by feedback to maintain constant power of discharge.

To check stoichiometry of films obtaining by the mode, two points on plot were chosen. The first point corresponds \( F = 0.3 \) and \( Q = 0.42 \) sccm, the second point corresponds \( F = 1 \) and \( Q = 1.4 \) sccm. One hundred nanometer thick films were grown for each of points. Then films composition were measured by Oxford Instruments X-Max 20 mm\(^2\) EDS device mounted on JEOL-6510 LV SEM. Measurement results are in table 1.

| \( F \) | \( O, \% \) | \( Ti, \% \) | \( O/Ti \) |
|---|---|---|---|
| 0.3 | 62.37 | 37.63 | 1.66 |
| 1 | 66.48 | 33.52 | 1.98 |
O/Ti rate at F = 1 actually should be equal 2. The observed deviation is caused by the error of measurement technique.

4. Conclusions

Obtained results show that compact magnetron facilities equipped with vacuum pumps with pump rates under 500 l/s are able to produce non-stoichiometric compounds. Moreover, volumetric flows of sputtering and reactive gases under these conditions are significantly less than in work [5]. That fact leads to cost reduction of industrial production of such compounds without decreasing of its efficiency.

O/Ti rate at F = 0.3 obtained in actual work is equal 1.66 and it slightly differs from O/Ti rate in [5]. Difference is caused by relatively high drift of discharge voltage at constant power maintenance and by EDS method error.

References

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