ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 22, No. 2. 2016

Reactive Sputter Deposition of $NiCr_xO_y$ Films Using NiCr Target

He YU [1], Tao WANG [1] *, Xiang DONG [1], Yadong JIANG [1], Roland WU [2]

[1] *School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, P. R. China*
[2] *Center for Plasma Material Interaction, Department of Nuclear, Plasma and Radiological Engineering, University of Illinois at Urbana-Champaign, IL, 61801, USA*

crossref http://dx.doi.org/10.5755/j01.ms.22.2.8563

Received 27 October 2014; accepted 25 January 2015

In this paper an original numerical model, based on the standard Berg model, was used to simulate the growth mechanism of $NiCr_xO_y$ deposited with changing oxygen flow during reactive sputter deposition. The effect of oxygen flow rate on the discharge voltage, deposition rate and the material elementary composition were investigated. The ratio of Ni and Cr content in the film was measured using energy-dispersive X-ray spectroscopy (EDX). EDX detected a decrease in the Cr concentration with the increasing of oxygen flow rate due to the preferential oxidation of Cr to Cr_2O_3. Results show a reasonable agreement between numerical and experimental data.

Keywords: numerical model, $NiCr_xO_y$, reactive sputtering, EDX.

1. INTRODUCTION

Nickel oxide and chromium oxides are frequently used in fields requiring a strong absorption in the visible range like electrochromic coatings and solar selective absorbers [1 – 2]. The interest for electrchromic material is based on their potential applications to e. g. smart windows, glare free and variable reflectance mirror and gas sensors [3 – 4]. Besides these applications, new technologies based on renewable energies, and in particular of solar energy, are undergoing a fast development. Among potentially attractive solar selective coatings, nickel chromium oxide thin films become more and more attractive for the researchers due to their high absorptance. Although the properties of nickel and chromium oxide layers have been studied [5 – 7], mixed oxide layers such as $NiCr_xO_y$ have received to date very little attention.

The film properties are known to be strongly dependent on the deposition parameters. The electronic and optical performance of $NiCr_xO_y$ is relative to the structure of the thin films. A slight change in the film composition can lead to very different optical constants of the material [8]. Moreover, the reproducibility and stability of electrical properties are dependent on the ratio of Ni and Cr element in the film. Hence, understanding of the influence of process parameters on the film composition is quite necessary.

In this paper, we present a model that enables us to predict film composition of $NiCr_xO_y$ prepared by reactive sputtering. Based on this model, the effect of oxygen concentration on the films composition was discussed. In the experimental part, we report $NiCr_xO_y$ thin films deposited by magnetron sputtering method with different oxygen flows and investigate the changing fraction of Ni and Cr with respect to the oxygen flow using EDX analysis. Moreover, the influence of O_2 flow rate on the reactive deposition parameters (deposition rate, target voltage) was systematically studied.

* Corresponding author. Tel.: +86-028-83207086;
fax: +86-028-83206123. E-mail address: *wtwhuestc@163.com* (T. Wang)

2. MODEL

The mathematical model describing the sputtering system is shown in Fig. 1. The total input rate of the reactive gas (oxygen) is denoted as Q_{tot}. In this paper, it is assumed that the film structure is a mixture of Ni, NiO, Cr, and Cr_2O_3. The fractions of Ni, NiO, Cr, Cr_2O_3 at the target will be called θ_{t1}, θ_{t2}, θ_{t3}, and θ_{t4}, respectively. θ_{s1}, θ_{s2}, θ_{s3}, θ_{s4} fractions are collecting area covered by Ni, NiO, Cr, Cr_2O_3, respectively (see Fig. 1).

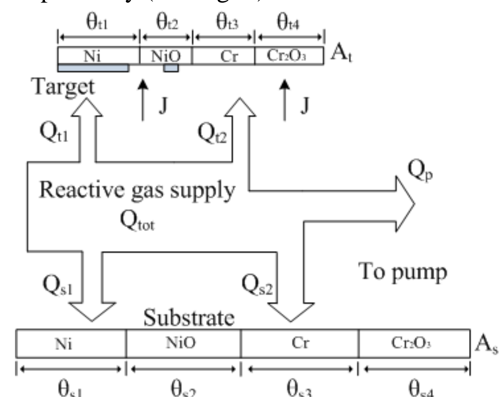

Fig. 1. Schematic of the conditions at NiCr alloy target and collecting area during reactive sputtering

It is assumed that the gettering of reactive gas onto metal nickel and chromium contributes the formation of NiO and Cr_2O_3 on the target respectively, which will increase θ_{t2} or θ_{t4}, respectively. For the metal Ni sputtered from the target, if the atom comes from the fraction of θ_{t1} and deposits on the substrate surface which previously consisted of NiO, then the fraction of Ni will increase and the fraction of the other compositions will decrease. Furthermore, when the compound of NiO sputtered from target deposit on the substrate which previously consisted

of Ni, Cr or Cr_2O_3, then the corresponding fraction of θ_{si} (i!=1) will decrease and the fraction of NiO will increase. However, the fraction of flux $\frac{J}{q}Y_{ti}\theta_{ti}A_t$ deposited onto the fraction θ_{si} of the collecting area A_s will not change the value of θ_{si}.

2.1. Conditions at the target surface

By making the assumptions above, and in combination with the simplifications presented earlier, the balance equations for the conditions on the target should be rewritten as the following:

$$\frac{J}{q}Y_{t2}\theta_{t2}A_t = 2\alpha_1 FA_t\theta_{t1}/l_1, \tag{1}$$

where J is the ion-current density, q is the elementary electronic charge. α_1 is the probability (sticking coefficient) for a oxygen molecule to react with a Ni atom that comes from the θ_{t1} fraction of the target. l_1 is the stoichiometry of NiO. A_t is the target area. F represents oxygen molecules/ unit area and time.

Eq. 1 determines the balance of the Ni atom fraction (θ_{t1}) on the target. For simplicity, the sputtered material from the surface fraction $\frac{J}{q}Y_{t2}\theta_{t2}A_t$ is assumed to be sputtered as molecules, irrespective of whether the material is ejected in atomic or molecular form. The only way sputtered compound molecules may be replaced is by reactions between neutral reactive gas molecules and Ni atoms.

$$\frac{J}{q}Y_{t4}\theta_{t4}A_t = 2\alpha_2 FA_t\theta_{t3}/l_2 \cdot \tag{2}$$

Moreover, Eq. 2 determines the balance of the fraction of θ_{t3} on the target. Here, l_2 is the stoichiometry of the Cr_2O_3. The reaction between Cr atoms and oxygen molecule will contribute to a decrease in the value of θ_{t3}. On the other hand, the compound Cr_2O_3 are sputtered from the surface fraction θ_{t4} and that will increase the fraction of θ_{t3}. Also note that all the compound fraction sums to unity (Eq. 3). An expression for A can be formulated in Eq. 4, which states that A is equal to the ratio between the total amount of Ni and Cr atoms on the target.

$$\theta_{t1}+\theta_{t2}+\theta_{t3}+\theta_{t4}=1; \tag{3}$$

$$(\theta_{t1}+\theta_{t2})/(\theta_{t3}+\theta_{t4}) = A\,. \tag{4}$$

2.2. Conditions at the substrate surface

At steady state, the contributions supporting an increase in θ_{si} must be identical to the contributions that support a decrease in θ_{si}. This leads to the following balance equations (Eq. 5 – Eq. 8) for the collecting area A_s.

Eq. 5 determines the balance of the fraction θ_{s2} on the substrate. The fraction of flux $\frac{J}{q}Y_{t2}\theta_{t2}A_t$ that deposited onto the fraction of Ni, Cr or Cr_2O_3 will increase the fraction of θ_{s2}. Obviously, the reactions between O_2 and Ni atoms at the substrate surface will increase θ_{s2}. The fraction of flux $\frac{J}{q}(Y_{t1}\theta_{t1}+Y_{t3}\theta_{t3}+Y_{t4}\theta_{t4})$ deposited onto the fraction (θ_{s2}) will contribute to a decrease in θ_{s2}.

$$\frac{J}{q}Y_{t2}\theta_{t2}A_t(1-\theta_{s2})+2\alpha_1 FA_s\theta_{s1}/l_1 = \frac{J}{q}(Y_{t1}\theta_{t1}+Y_{t3}\theta_{t3}+Y_{t4}\theta_{t4})\theta_{s2}A_t \cdot \tag{5}$$

Similar to the above, the steady-state equation for the fraction of Cr and Cr_2O_3 on the substrate may therefore be defined as:

$$\frac{J}{q}Y_{t3}\theta_{t3}A_t(1-\theta_{s3}) = \frac{J}{q}(Y_{t1}\theta_{t1}+Y_{t2}\theta_{t2}+Y_{t4}\theta_{t4})\theta_{s3}A_t + 2\alpha_2 FA_s\theta_{s3}/l_2; \tag{6}$$

$$\frac{J}{q}Y_{t4}\theta_{t4}A_t(1-\theta_{s4})+2\alpha_2 FA_s\theta_{s3}/l_2 = \frac{J}{q}(Y_{t1}\theta_{t1}+Y_{t2}\theta_{t2}+Y_{t3}\theta_{t3})\theta_{s4}A_t \cdot \tag{7}$$

Finally, the sum of fractions (θ_{s1}, θ_{s2}, θ_{s3}, θ_{s4}) is equal to 1, as in the case of the target surface.

$$\theta_{s1}+\theta_{s2}+\theta_{s3}+\theta_{s4}=1\,. \tag{8}$$

Therefore, compound formation by reaction between oxygen molecules and Ni, Cr at the target will consume reactive gas molecules Q_{t1}, Q_{t2} reactively. The consumption (number of oxygen molecules per unit time) at the target Q_{ti} can be obtained from Eq. 9.

$$Q_{t1} = 2\alpha_1 FA_t\theta_{t1}/l_1; \quad Q_{t2} = 2\alpha_2 FA_t\theta_{t3}/l_2; \quad Q_t = Q_{t1}+Q_{t2}\,. \tag{9}$$

While the consumption Q_{si} at the collecting area A_s can be expressed by Eq. 10

$$Q_{s1} = 2\alpha_1 FA_s\theta_{s1}/l_1; \quad Q_{s2} = 2\alpha_2 FA_s\theta_{s3}/l_2; \quad Q_s = Q_{s1}+Q_{s2}\,. \tag{10}$$

The remaining part Q_p of the reactive gas will escape from the processing chamber through the pumping system.

$$Q_p = \frac{PN_a}{R_r T}S\,. \tag{11}$$

The total supply rate of the reactive gas is denoted Q_{tot}, where

$$Q_{tot} = Q_t + Q_s + Q_p\,. \tag{12}$$

3. EXPERIMENTAL

The $NiCr_xO_y$ coatings were deposited from a NiCr target by DC reactive magnetron sputtering. The deposition chamber was evacuated to a base pressure of about 1.0×10^{-4} Pa by a combination of turbomolecular and rotary vane pumps. In order to ensure reproducible results of the reactive sputtering between runs, the NiCr target was first pre-sputtered by argon plasma for 15 min, and then oxygen injection was kept on for 15 min until the equilibrium reached in the argon/oxygen mixture. Argon and oxygen flow were controlled by using independent mass flow controllers, the argon flow was kept constant at 100 sccm and the oxygen flow was varied from 1.0 to 6.0 sccm. Before the substrates were mounted on a substrate holder, they were ultrasonically cleaned in acetone, ethanol and de-ionized water for 20 min sequentially, and then dried by pure nitrogen stream. For all the experiments, two steps were applied: cleaning of the NiCr target surface by pre-sputtering of 15 min in a pure argon atmosphere, followed by reactive deposition of $NiCr_xO_y$ films for around 25 min. The substrate holder was rotated at 10 rpm to ensure uniformity of film deposition and there were no intentionally h+eating during experiment. So the deposition temperature is 300 K.

4. RESULTS AND DISCUSSION

As the values of the sputtering yields are crucial input parameters for the calculation of sputter yield, a binary collision approximation (BCA) has been used in this work. BCA is routinely used to describe ion/solid interaction for sputtering yield calculations. In this work, the program Transport of Ions in Matter (TRIM) from The Stopping and Range of Ions is Matter (SRIM [9]) 2006 package was used. TRIM is a static program, where the target composition is fixed and not influenced by ion bombardment. TRIM calculations give the sputter yields of Ni and Cr are 1.62 and 1.44 for argon plasma with the ion energy of 400 eV.

From the above modeling, it is possible to calculate the fraction of Ni, Cr, NiO and Cr_2O_3 on the target as a function of oxygen flow, which was shown in Fig. 2.

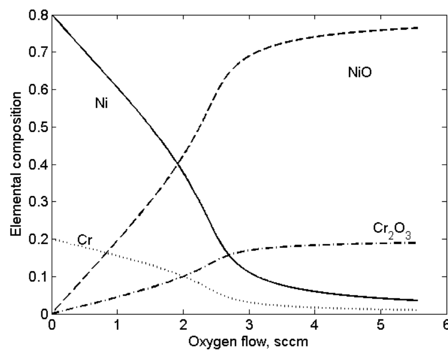

Fig. 2. Calculated results for fraction of Ni, NiO, Cr and Cr_2O_3

In the modeling section, the input parameter of initial ratio of Ni and Cr element on the target is 4:1. It indicates that the initial fraction of Ni and Cr are 80 % and 20 %, respectively. The fractions of metal Ni and Cr decrease most rapidly for low reactive gas flow, but decrease asymptotically to zero for high flows. On the other hand, the NiCr target was first pre-sputtered by argon plasma in the experiment. So, the target is assumed to be covered only by NiCr alloy for zero flow of oxygen in the modeling. Therefore, the fractions of NiO and Cr_2O_3 are equal to zero at the beginning of the curves. With the continued increasing amount of oxygen, the fractions of NiO and Cr_2O_3 increase dramatically in the region of 2 – 2.8 sccm, and gradually increase to the steady value. In the region up to 2 sccm, the fraction of NiO and Cr_2O_3 become higher than those of the corresponding metals. In the compound mode, the target surface is covered with a compound layer which has typically sputter rate much lower than the corresponding metal.

It is seen from Fig. 3 that the deposition rate decreases dramatically at oxygen flow of 2.5 sccm, corresponding to the point that fractions of oxides dramatically increase. In the reactive sputtering, the deposition rate is closely related to the sputtering yield of the target. However, when the oxygen flow is low, the sputtering process occurs in metallic mode. Also, the oxide formation rate on the target is lower than the sputtering etch rate of the material from the target, hence the sputtering yield usually keeps a high value close to non-reactive sputtering. As a result, the thickness of the film which contains a certain amount of oxygen will be larger than the pure metal or the one contain less oxygen, due to the volume expansion caused by the incorporation of oxygen into the film during deposition. Therefore, the oxide coverage area on the target surface will increase rapidly with lower oxygen flow.

When the oxygen flow exceeds a critical amount, more oxygen can react with the target and the oxide formation rate on the target surface will eventually exceed the etch rate of metal and oxide. An oxidized target will be formed and the sputtering occurs in oxide mode. Then the deposition rate is reduced significantly because NiO and Cr_2O_3 have considerably lower sputtering yield compared with that of metal Ni and Cr, respectively.

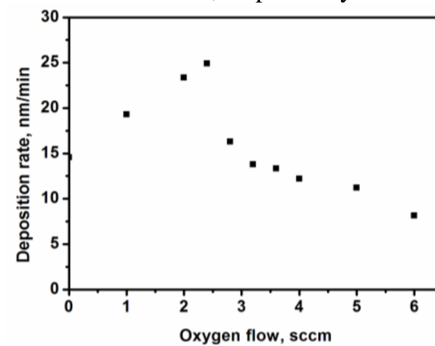

Fig. 3. Experimental mass deposition rate vs. the flow of oxygen

The abrupt transition from high rate metal mode to compound mode, with substantially lower mass deposition rate, occurs at a flow of 2.5 sccm of O_2. The transition is accompanied by an equally abrupt change in the discharge voltage, as shown in Fig. 4, due to a change of target surface composition.

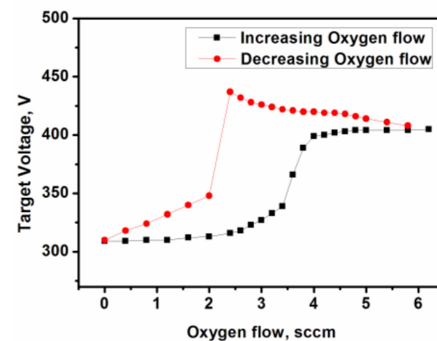

Fig. 4. Experimental results of target voltage vs. oxygen flow

In the reactive sputtering, the competition between the formation and erosion of the oxide on the target surface is strongly influenced by the oxygen flow rate. Many status parameters of the reactive sputtering process such as oxygen partial pressure, cathode voltage etc usually show a highly non-linear hysteresis. And the main reason for such phenomena can be explained as followed. when the oxygen flow below the critical amount, the formation rate of the oxide on the target surface usually lower than or equal to the sputtering etch rate, therefore the oxide coverage area on the target surface will increase gradually with the oxygen flow and so does the cathode voltage. But when the oxygen flow exceeds the critical amount, the oxide coverage area on the target surface will increase rapidly, and target will be fully oxidized eventually, which will cause an abrupt change of the cathode voltage. With the decrease of oxygen flow, the status of the target surface will not be changed immediately even the oxygen flow

lower than the critical amount, resulting in the hysteresis effect. Due to the different reactivity of Ni and Cr, and also the different ratios Y_{Ni}/Y_{Cr} (sputtering yield) of the targets, the film composition may vary quite dramatically as a function of the reactive gas supply O_{tot}. In Fig. 5, the metal ratios in the films as a function of oxygen flow rate are shown for the reactive sputtering of NiCr.

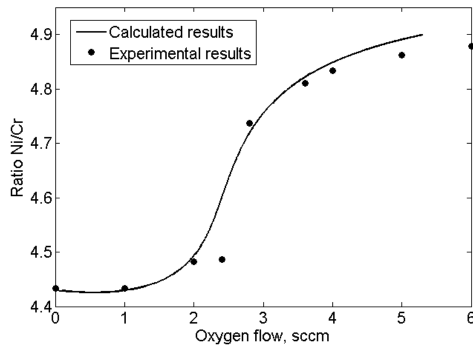

Fig. 5. Comparison between the metal ratios vs. oxygen flow supply obtained by experimental results and calculated results

For zero flow of oxygen, the target is covered by NiCr alloy. As we mentioned above, the initial area ratio of Ni and Cr on the target is assumed to be 4. Moreover, the sputter yields of Ni and Cr are given by 1.62 and 1.44, respectively. Thus, the initial ratios of Ni and Cr in the films are equal to $1.62 \times 4/1.44 = 4.5$. With the increasing amount of oxygen, the target surface is covered with the compound layers of NiO and Cr_2O_3 which have typically sputter rate much lower than the corresponding metals. According to the results in Ref [10 – 11], Cr is preferentially oxidized to Cr oxide on a NiCr alloy surface and Ni in the alloy reacts with oxygen more slowly than the Cr. Normally, the sputter yields of oxides are far less than those of metals. The ratio between the total amount of Ni and Cr on the target is constant. Therefore, the average sputter yield of Cr element ($Cr + Cr_2O_3$) becomes lower than that of Ni element (Ni + NiO), resulting in the reduction of ratio of Cr element and Ni element in the film. It is seen that the trends in the experiments are adequately described by the simulations. Therefore, the model can be used to find optimum processing conditions for deposition of $NiCr_xO_y$ films of a desired element ratio.

5. CONCLUSION

In this article, the reactive sputter deposition of $NiCr_xO_y$ was investigated by both numerical modeling and experiments at different reactive gas flow. The reactive sputtering behaviours of the targets such as target voltage and mass deposition rate have been explained from the sputter yields of Ni and Cr. The influence of O_2 flow rate on the reactive deposition parameters (deposition rate, target voltage, material elementary composition) was systematically studied.

The metal ratios of Ni and Cr respect to the oxygen gas flow employed in the numerical model were confirmed by EDX. Results show a reasonable agreement between numerical and experimental data. Increasing the O_2 flow rate, EDX detected a decrease in the Cr element concentration. It is because that the Cr on the target tends to react with oxygen more easily than Ni.

Acknowledgments

This work was partially supported by the National Science Foundation of China (NSFC) Grant Nos. 61405027, 61405025, 61405026, 61421002 and 61235006. It was also supported by the Postdoctoral Science Foundation of China (Grant No. 2014M562296) and the Fundamental Research Funds for the Central Universities (Grant No. ZYGX2015J045).

APPENDIX A

The following simulation parameters were used in the work: $\alpha_1 = 0.8$, $\alpha_2 = 0.8$. $l_1 = 2$, $l_2 = 3$. Target area $A_t = 260$ cm^2, gas temperature $T = 300$ K, pumping speed $S = 0.2$ m^3/s.

REFERENCES

1. **Li, S., Liu, M., Bi, H., Liya, L., Wenqin, Z., Huang, Z., Du, Y.** The Enhanced Magnetic Properties of Ni Nanocrystallites Induced by the Coupling between Ni/NiO Interfaces *Journal of Alloys and Compounds* 425 (1 – 2) 2006: pp. 1 – 3.
2. **Huang, X., Tu, J., Zhang, B., Zhang, C., Li, Y., Yuan, Y., Wu, H.** Electrochemical Properties of NiO-Ni Nanocomposite as Anode Material for Lithium Ion Batteries *Journal of Power Sources* 161 (1) 2006: pp. 541 – 544.
3. **Gaouyat, L., Mirabella, F., Deparis, O.** Vanadium Oxide Thin Films Deposited on Indium Tin Oxide Glass by Radio-Frequency Magnetron Sputtering *Chinese Physics B* 11 (7) 2002: pp. 737 – 740. http://dx.doi.org/10.1088/1009-1963/11/7/317
4. **Granqvist, C.** Oxide Electrochromics: An Introduction to Devices and Materials *Solar Energy Material & Solar Cells* 99 2012: pp. 1 – 13. http://dx.doi.org/10.1016/j.solmat.2011.08.021
5. **Hotovy, I., Buc, D., Hascik, S., Nennewitz, O.** Characterization of NiO Thin Films Deposited by Reactive Sputtering *Pergamon* 50 (1 – 2) 1998: pp. 41 – 44.
6. **Hotovy, I., Huran, J., Janik, J., Kobzev, A.** Deposition and Properties of Nikel Oxide Films Produced by DC Reactive Magnetron Sputtering *Pergamon* 51 (2) 1998: pp. 157 – 160.
7. **Sato, H., Minami, T., Takata, S., Yamada, T.** Transparent Conducting P-type NiO Thin Films Prepared by Magnetron Sputtering *Thin Solid Films* 236 (1 – 2) 1993: pp. 27 – 31.
8. **Zhao, S., Wackelgard, E.** Optimization of Solar Absorbing Three-layer Coatings *Solar Energy Material & Solar Cells* 90 (3) 2006: pp. 243 – 261. http://dx.doi.org/10.1016/j.solmat.2005.03.009
9. **Petrovic, S., Bundaleski, N, Radovic, M., Ristic, Z., Gligoric, G., Perusko, D., Zec, S.** Structure and Surface Composition of NiCr Sputtered Thin Films *Science Sintering* 38 2006: pp. 155 – 160. http://dx.doi.org/10.2298/SOS0602155P
10. **Jeng, S., Holloway, P., Asbury, D., Hoflund, G.** Changes Induced at Ni/Cr Alloy Surfaces by Annealing and Oxygen Exposure *Surface Science* 235 (2 – 3) 1999: pp. 175 – 185.