STUDY OF reactive gas modulation in reactive magnetron sputtering of NiO thin films

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Abstract

We present the pulsed dc magnetron sputtering method in which a nickel target is sputtered in a mixture of argon and reactive gas oxygen. The flow modulation of oxygen is proposed to enhance the deposition process of preparation of the oxide films. The flow rate of oxygen is modulated periodically in time and during deposition when oxygen flows is cut off to remove the oxide formed on the target. Modulated deposition process was monitored directly by optical emission spectroscopy, the deposition rate and partial pressure measurement. The effect of the different oxygen flow periodically changes in time on the selected Ni and O2 emission intensities and the deposition rate were investigated. The variations of atomic ratio in NiO films were revealed by SIMS method.

6. Introduction

Nickel oxide (NiO) thin films have been applied in electrochromic devices, as p-type transparent conducting films an as sensitive material for the various gas sensors because their chemical stability as well as optical and electrical properties are excellent. These films have been fabricated by the different physical and chemical vapour deposition techniques. Among these methods the reactive magnetron sputtering is widely used in preparation of NiO thin films. Reactive sputter deposition involves the sputtering of metal, alloy or compound in a reactive gas mixture in order to deposit a compound film composed of the sputtered material and the reactive species. A wide variety of compounds have been formed in this way, with a wide range of properties. In this method, it is well known that the deposition can be unstable due to the competition between the target sputtering and the consumption of the reactive gas either by target or by the deposited film.

We present the pulsed dc magnetron sputtering method in which a nickel target is sputtered in a mixture of argon and reactive gas oxygen. The flow modulation of oxygen is proposed to enhance the deposition process of preparation of the oxide films [1]. The flow rate of oxygen is modulated periodically in time and during deposition when oxygen flows is cut off to remove the oxide formed on the target [2, 3]. This leads to oscillating oxygen
concentration during the sputtering process and causes the variation of the atomic ratio in growing film.

2. Experiment

The experiments were carried out in the experimental apparatus (Fig. 1) which contained of a dc custom-built magnetron sputtering source with a Ni target. Measurements of flow conditions were realized at constant total pressure of the working mixture and its value was 0.5 Pa. The oxygen flow rate was regulated with computer operated experimental unit in conjunction with a mass flow controller. The flow rate of oxygen was modulated periodically in time. During one period (50 s), first, oxygen flow was on 45 s and second, O\(_2\) flow was cut off (5 s). The discharge power was maintained at 600 W.

The light emitted from discharge was collected from a certain point near the target by two UV lenses and 1 mm aperture (mounted in between) onto the entrance slit 0.3 m monochromator Bentham M300E. A photomultiplier Hamatsu R955 was mounted just behind the exit slit of the monochromator. The photomultiplier signal was sent to current supply, then to analogue-digital converter and the spectra stored on a microcomputer. This optical system was mounted upon a vertically moving table, which enables us to observe the emitted light from plasma along the target. The spectral range between 300 and 900 nm was investigated. In order to study the influence of oxygen flow 10, 30 and 50 sccm, respectively, on the OES spectra we selected Ni (352.4 nm), Ar (751.4 nm) and O (777.0 nm) lines on which to focus. Partial pressure measurements were realized at the constant values of pumping speed and of chamber volume by a capacitance manometer (MKS Baratron). The changes of deposition rates were monitored by a thin film thickness and deposition rate monitor (Inficon) with a quartz crystal sensor head. A quadrupole SIMS instrument Physical Electronics PHI ADEPT 1010 with primary ion beam Cs\(^+\) was used to depth compositional analysis of NiO films prepared by this process.

3. Experimental results

In our previous study were defined the sputtering modes for continuous addition of oxygen at NiO deposition [4]. According to these results were chosen the oxygen flow rates. The conditions of the oxygen flow rates and period in Fig. 2a were respectively 10 sccm and 50 s, 30 sccm and 50 s, 50 sccm and 50 s. The first condition corresponds to the experimental observation for metal-sputtering mode while the other conditions are valid for oxide-sputtering mode for the continuous addition of oxygen. The figures help to characterize the effects of the oxygen modulation on the parameters and the properties of sputtering process.

In Fig. 2b the modulation causes the oscillation of oxygen partial pressure. The partial pressure measurements were realized at the constant values of pumping speed and of chamber volume without plasma. Fig. 2b shows the change of the partial pressure of oxygen during an oxygen-on and oxygen-off period for various oxygen flows. The time for increase and decrease of the partial pressure is determined by pumping speed, chamber volume and oxygen flow. Using the modulation unit we controlled oxygen flow and this lead to an oscillating oxygen concentration during the sputtering process. When the oxygen flow is cut off, the partial pressure will be decreased and the decrease in the partial pressure will enhance the deposition rate.

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Fig. 1: Block schema of the experimental apparatus: 1) - vacuum pumping system, 2) - vacuum chamber, 3) - quartz window, 4) - magnetron sputtering source with Ni target, 5) - carrousel holder of samples, 6) - carrier of substrates, 7) - shield, 8) - shield operator, 9) - step engine, 10) - bias, 11) - Pirani gauge, 12) - needle valve, 13) - mass flowmeter, 14) - mass flowmeter, 15) - LN₂ trap, 16) - total pressure controller, 17) - optical system, 18) - monochromator, 19) - current amplifier, 20) - PC, 21) - modulation unit, 22) - power supply

OES yields interesting information on excited species, atoms, molecules and radicals present in the plasma as well as qualitative variations of these species with respect to the discharge conditions. The corresponding variations of the intensities of Ni (352.4 nm), O (777.0 nm) and Ar (751.4 nm) lines against the oxygen flow rate are given in Fig. 3. We note that the changes are due to the oxygen modulation and they reflect the coverage of the target. During the oxygen-off period the peak intensity from Ni line rapidly increases while the oxygen OES signal indicating the concentration of excited oxygen molecules in the plasma decreases.

The variations of the target voltage (Fig. 4) show the regions correspond to the three regimes: 1) oxide-sputtering mode with low value of the target voltage (318-325 V), 2) transition-sputtering mode characterized by an abrupt increase in the value of the target voltage, 3) metal-sputtering mode when the discharge voltage increases to 430-440 V. In the oxide-sputtering mode the poisoning of the target becomes serious because of the higher secondary electron emission coefficient of the oxide compared to that of pure metal, the total number of electrons near the target increases and hence higher target current can be achieved at lower voltage.

Some samples on silicon substrates have been deposited by repeated oxygen-on and oxygen-off cycles. In the case of sample prepared at 10 sccm oxygen flow rate (Fig. 5) the
SIMS depth profiling show that the level of Ni and O is constant and is not affected by periodic oxygen addition. On the other hand, SIMS measurements from samples prepared 30 and 50 sccm oxygen flow rate clearly record the oscillation of Ni and O in the depth profile (Fig. 6).

Fig. 2: (a) Schematic representation of pulsed oxygen flow rate and (b) partial pressure of oxygen in deposition chamber during an oxygen-on and oxygen-off period at the different oxygen flow. Total pressure was 0.5 Pa.

Fig. 3: Time dependencies of OES signals of nickel, oxygen and argon for periodic oxygen addition (a) 30 sccm, (b) 50 sccm.
Fig. 4: (a) Time variation of the deposition rate experimentally observed and (b) real time measurements of nickel target potential for periodic oxygen addition.

Fig. 5: SIMS depth profile taken from NiO film prepared at 10 sccm oxygen flow.
Fig. 6: SIMS depth profile taken from NiO film prepared at 50 sccm oxygen flow.

4. Conclusion

A sputtering process to enhance and change the deposition rate of NiO in reactive magnetron system was proposed using flow modulation of oxygen. This study also concluded that this process can be used for control of deposition film compositions. By this process thin NiO films with the different oxygen content can be deposited alternatively and the multilayered film results.

Acknowledgement

The work was supported by Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences, No. 1/7614/20 and by Royal Society, UK.

References