Preparation of Metal Oxides Thin Films by Hollow Cathode Plasma Jet

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Abstract. The purpose of this work was to present review of preparation of metal oxides thin films by hollow cathode plasma jet as well as first result of depositing Ni, Cu and NiCu oxide films for the oxidation of volatile organic pollutants with the idea of further application of these films for air purification.

Introduction

Metal oxide thin films have been used in semiconductor devices, solar cells, transistors, photoelements, protect coating, catalyst. Among plasma methods of creating such films, magnetron sputtering and a hollow cathode are most commonly used.

Recently, Olejníček et al. [2019] investigated the deposition of metal oxide films by different plasma sputtering techniques. Semiconducting crystalline Co3O4 thin films were prepared employing three methods: radiofrequency magnetron (RF) sputtering, high-power impulse magnetron sputtering (HiPIMS) and hollow cathode discharge (HCD). Results shown that HCD allows to obtain higher porosity, higher electrical resistance, higher activation energy, and higher deposition rate during the sputtering process, which contributes to an increase in the efficiency of the film formation process and improves the quality of the film itself, since high porosity means a larger active surface.

SEM images of Co oxide films deposited on stainless-steel substrate are shown in Fig. 1. The film obtained by RF magnetron sputtering repeated the structure of stainless-steel substrate. The HiPIMS sample showed a smoother surface compared to the substrate itself. The authors note that a possible reason for this may be the high ionization fraction of depositing particles. The principle is as follows: the electric field on the surface of the substrate (it is stronger at the sharp edges) attracts ionized particles of inert gas and sputtered atoms and in addition a stronger electric field at the edges causes a stronger bombardment of these areas, and as a result re-sputtering of the deposited atoms can occur.

The films prepared using the hollow cathode discharge have a porous nanocrystalline structure with spherical objects up to 400 nm in size. The main reason for the porosity, according to the authors, is that inert gas flowing through the hollow cathode causes higher pressure (more than 100 Pa) inside the nozzle compared to the magnetron plasma operating at pressures \( \approx 1 \) Pa. Under such conditions, nanoclusters of sputtered material are formed inside the hollow cathode, which settle on the substrate together with individual atoms. In addition, at higher pressures, the mean free path of the particles is 10 times less than for magnetron sputtering. After annealing (applied to deposited film to support formation of crystallization of the film) facets appeared on all surfaces, with the largest size for the RF magnetron and the smallest for HiPIMS.

Semiconducting crystalline films of non-stoichiometric WO3 and WO3-x thin films were prepared by the hollow cathode plasma jet [Olejníček et al., 2022]. Fig. 2a shows as-deposited (not annealed)
WO$_{3-x}$ samples for different oxygen gas flows. Annealing was carried out at 450 °C for 4 hours to increase the O/W ratio in films. Since the authors were interested in photoactivity of deposited thin films, they investigated an effect of increasing oxygen mass flow rate during the deposition process on transparency of the films. The results demonstrated that increase in the oxygen mass flow rate leads to change of the film color through brown, blue to fully transparent. An annealing of these samples in air led to color loss: blue sub-stoichiometric WO$_{3-x}$ films changed to fully transparent WO$_3$ material. The spectral transmittance of as-deposited films abruptly changes for samples with upper then 40 sccm of oxygen mass flow rate. Also, the oxygen mass flow rate has impact on surface morphology (Fig 2b). Adding more oxygen leads to the smoother surface. But because a higher oxygen flow means higher deposition rate these three samples have different thickness — 180, 400 and 470nm.

Delahoy et al. [2005] reported the production of transparent and semi-transparent films using a hollow cathode in a reactive mode. Since only inert gas flows through the hollow cathode the sputtering occurs always in a metallic mode — the hollow cathode isn’t oxidized because reactive gas enters a depositing chamber by an external port. Doped oxide thin films are produced by using hollow cathode made of one metal and the second target for doping, which allow changing the amount of the doped element. The equipment scheme is shown in Fig. 3a. The target for doping was a metal wire, which was located immediately behind the hollow cathode and parallel to its major axis (not shown in the figure).

Transparent conducting oxides such as dopped semiconductor In$_2$O$_3$, ZnO, and SnO$_2$ are most often used as a part of photovoltaic cell. The main requirements for such materials are high conductivity and high optical transmission (especially infrared transmission). The properties of the obtained films are shown in table in Fig. 3b.

The mobility of charge carriers of non-doped films was 11.5 (for deposition at temperature 120 °C) and 38.5 cm$^2$/Vs (for deposition at temperature 260 °C). The highest mobility for doped films showed In$_2$O$_3$: Ti and In$_2$O$_3$: Mo, which were equal to 80.6 and 80.3 cm$^2$/Vs, respectively. These films also showed the lowest electrical resitivity. The film In$_2$O$_3$:Ti also had a high transmission.

Besides, Delahoy et al. [2016] used a two-hollow cathode system to produce aluminum-doped ZnO, ZnO$_x$N$_y$ and Cd$_x$Sn$_{1-x}$O. Second cathode was perpendicular to the first one. Control of the oxygen partial pressure allowed to obtain the films with different transmission and resistivity (Fig. 4). The authors managed to get as-deposited ZnO: Al film with mobility 53.4 cm/Vs (previously obtained mobility was 7–57 cm$^2$/Vs for as-deposited aluminum-doped ZnO by sputtering method).
Experiment and results

The first attempts of depositing metal oxide thin films by hollow cathode discharge were produced with a direct current (DC) power supply. The hollow cathode was a cylindrical nozzle made of the appropriate composition of copper and nickel (Kurt J. Lesker, Inc. for all metals and alloys, purity 99.95%). The cathode was powered in a constant voltage regulation mode. The total discharge power was 600 W, and the discharge current was 2 A. Films were prepared on Si (100) substrates, and during deposition the temperature of the sample was below 150 °C.
Deposition chamber (see Fig. 5) for the preparation of these samples is the same as in work of Olejniček et al. [2019] and is described here in detail. The hollow cathode was a nozzle made of pure nickel, pure copper or an alloy of nickel and copper (there were three kinds of alloy: 1 — 20 % Cu and 80 % Ni; 2 — 50 % Cu and 50 % Ni; 3 — 80 % Cu and 20 % Ni). These metals were chosen because their oxides (as well as transition metal oxides in general) are applicable to the creation of oxidation catalysts, where volatile organic pollutants on the catalyst surface are converted to water and carbon dioxide. Processing gases such as argon (mass flow rate 150 sccm) and oxygen (mass flow rate 200 sccm) were fed into the chamber. The inlet of argon was through the nozzle, and oxygen was fed from the other inlet for the production of metal oxides films. The pressure during the deposition process was 5 Pa and 80 Pa, under constant others conditions.

Comparison of SEM images of deposited thin films (see Fig. 6) showed that under the pressure of 80 Pa increasing amount of Cu particles in the film had impact on thin films morphology changing from the surface with inclusion cracks (islands) to the rough nanostructured surface. At a pressure of 5 Pa, for the composition Cu 50 % Ni 50 % and Cu 80 % Ni 20 %, cracks disappeared. Also, at a pressure of 80 Pa, only the composition Cu 50 % Ni 50 % showed a surface almost without cracks, in contrast to other compositions. Since the larger the surface area of the catalyst, the more efficient its operation will be, in the future it is planned to measure the roughness of the films using AFM.

X-ray diffraction measurements (see Fig. 7) of samples obtained with the pure Ni, and alloy Cu 20 % Ni 80 %, and Cu 50 % Ni 50 % nozzles showed the appearance of NiO (200) peak at 80 Pa whilst peak corresponding NiO (111) appeared at pressure 5 Pa [Richardson et al., 2003]. Both diffraction peaks were significantly suppressed for nozzle alloy Cu 50 % Ni 50 %.

Figure 6. SEM images Ni-containing oxides films. (a) Ni nozzle, 80 Pa; (b) Cu 20 % Ni 80 % nozzle, 80 Pa; (c) Cu 50 % Ni 50 % nozzle, 80 Pa; (d) Cu 80 % Ni 20 % nozzle, 80 Pa; (e) Cu nozzle, 80 Pa; (f) Ni nozzle, 5 Pa; (g) Cu 20 % Ni 80 % nozzle, 5 Pa; (h) Cu 50 % Ni 50 % nozzle, 5 Pa; (i) Cu 80 % Ni 20 % nozzle, 5 Pa; (j) Cu nozzle, 5 Pa.

Figure 7. XRD images Ni-containing oxides films deposited at 5 Pa and 80 Pa by hollow cathode discharge.
Conclusions

Obtained results proved that the deposition of metal oxides with a hollow cathode discharge is promising technique for preparation of thin film with enhanced morphology. Samples with thin films of NiO, Cu$_2$Ni$_8$O$_x$, Cu$_5$Ni$_5$O$_x$, Cu$_8$Ni$_2$O$_x$, and CuO, made by hollow cathode under the pressure 5 Pa, showed that the addition of 50 % Cu significantly changes surface morphology with comparing to case for nozzle of pure metal or alloy with additional material about 20 %.

References


