Armenian Journal of Physics, 2019, vol. 12, issue 1, pp. 62-77

Magnetron Sputtering Techniques and Their Applications at Gas Sensors Manufacturing

M.S. Aleksanyan,

Yerevan State University, 1 Alex Manoukian str., 0025, Yerevan, Republic of Armenia
E-mail: maleksanyan@ysu.am

Received 07 February 2019

Abstract. The types of thin film deposition techniques and their differences are presented in this article. The characteristics of magnetron sputtering techniques are thoroughly observed. A review of recent research efforts and developments for the fabrication of semiconductor resistive gas sensors using magnetron sputtering deposition methods, presenting its potential advantages as a materials synthesis technique for gas sensors along with a discussion of their sensing performance are also presented. It can be argued that these advantages are likely to drive increased interest in the use of magnetron sputtering techniques for gas sensor materials over the next decade as the advanced physical vapor deposition (PVD) method.

Keywords: deposition technology, magnetron sputtering, gas sensor, thin film, plasma

1. Introduction

Thin film deposition technology has a documented history of more than 5000 years. However, thin film growth by sputter deposition and chemical precipitation, which required the development of vacuum pumps, electrical power and chemical processing technology, is a comparatively recent phenomenon. First time for scientific purposes thin film deposition was carried out by Michael Faraday in 1857, which was reported. At that time Faraday obtained thin metallic films by exploding metal wires in a vacuum vessel [1-3].

Historically, the thin film deposition techniques have developed in approximately this sequence: thermally induced evaporation (by electrical resistance heating, induction heating and electron beam heating), sputtering (diode, triode, magnetron, ion beam sputtering), arc processes, and most recently, laser ablation. At the same time, the technology of chemical deposition has also developed: chemical vapor deposition, electro-deposition, atomic layer epitaxy and ultrasonic/polymer assisted deposition [4, 5].

Deposition technology can be considered as the key to the creation of basic computer, optical, gas sensor solid-state devices which are based on the different materials and structures. Thin films are now widely applied in everyday used electrical equipments. For example, thin films are used in the manufacturing of integrated circuits, in production of magnetic films, optical coatings, semiconductor metal oxide gas sensitive layers, electronic displays and so on. The key parameters of electronic devices are largely dependent on the quality, structure, and the deposition methods of thin films. Electronic engineers and scientists working in this area are making great efforts to improve the quality of thin film for solid-state devices and develop the deposition technologies. Year by year, equipment manufacturers successfully overcame more stringent requirements to improve deposition systems and to get cheaper and upgraded structures

making process monitors and controls for measuring film parameters. One of the most important reasons for rapid growth of thin film technologies over the past four decades was the remarkable advancement of analytical instrumentation that led to a conscious understanding of the physics and chemistry of films, surfaces, interfaces and nanostructure of systems [6, 7].

Gas detection and determining its composition and the concentration of gas mixtures are necessary in many different fields such as environmental monitoring, vehicle and industrial emission control, household security, food quality control, disease detection, alcohol breath test and so on. There are various methods to detect and analyze different gases including gas chromatography, Fourier-transform infrared spectroscopy, chemiluminescence detectors, mass spectrometry, semiconductor gas sensors and so on. Solid-state gas sensors based on different materials including inorganic metal oxide and organic semiconductors, have many advantages in comparison to other gas sensing methods. Mainly in metal oxide based sensors numerous metal oxide semiconductor materials, including both single $(ZnO, SnO_2, WO_3, TiO_2, Fe_2O_3, \text{etc.})$ and multi-component $(BiFeO_3, MgAl_2O_4, SrTiO_3, Sr_{1-y}Ca_yFeO_{3-x}, \text{etc.})$ oxides, are used as the active layers. Solid-state gas sensors have been widely studied and used due to their low costs, easy to miniaturize and production, high sensitivity, selectivity, stability and reliability. All these parameters are largely dependent on the quality of thin or thick films used in gas sensors. The chosen technology mostly determines the main characteristics of gas sensors: the morphology, the homogeneity, the thickness, the granular structure, the price and so on. Therefore it is extremely important to choose the right technology to obtain solid-state gas sensors with acceptable parameters [8-10].

In this study, the thin film deposition technologies and their specifications used in the production of gas sensors are thoroughly investigated. Mainly we are focused on the discussion of the magnetron sputtering techniques and its features as one of the advanced methods for obtaining gas sensing layers.

2. Thin film deposition techniques

There are dozens of deposition technologies for obtaining thin and thick films by various materials. They are divided into two large groups that are fundamentally different from each other: physical deposition and chemical deposition. These two deposition methods also have different types that have own technological features.

Table 1. The technological modes for film deposition and formation.

Physical Deposition		**Chemical Deposition**	
Sputtering	**Evaporation**	**Gas phase**	**Liquid phase**
Glow discharge DC sputtering	Vacuum evaporation	Chemical vapor deposition	Electro-deposition
Triode sputtering	Resistive heating	Laser chemical vapor	Chemical bath deposition (CBD)/ arrested precipitation

	evaporation	deposition	technique (API)
Getter sputtering	Flash evaporation	Photo-chemical vapor deposition	Electro less deposition
Radio frequency sputtering	Electron beam evaporation	Plasma enhanced vapor deposition	Anodisation/ molecular beam epitaxy/liquid phase epitaxy
Magnetron and ion beam sputtering	Laser evaporation	Metal-organic chemical vapor deposition (MOCVD)	Sol-gel/Spin coating/ Spray-pyrolysis technique
A.C. Sputtering	Arc and R. E. Heating	Atomic layer epitaxy (ALE)	Ultrasonic (SPT)/ polymer assisted deposition

The physical deposition method is divided into two main groups: sputtering and evaporation. The chemical deposition method is also divided into two main groups: deposition by gas phase (Chemical Vapor Deposition-CVD) and deposition by liquid phase. The more important technological modes for thin film deposition and formation are categorized in Table 1 [1, 11].

In physical deposition processes the film deposition takes place by physically movement of material from target to the substrate [12]. There are no chemical reactions which form or synthesize the material. In chemical deposition the creation of solid material takes place by directly chemical reactions in gas or liquid compositions forming new material on the substrate (see Fig. 1) [13].

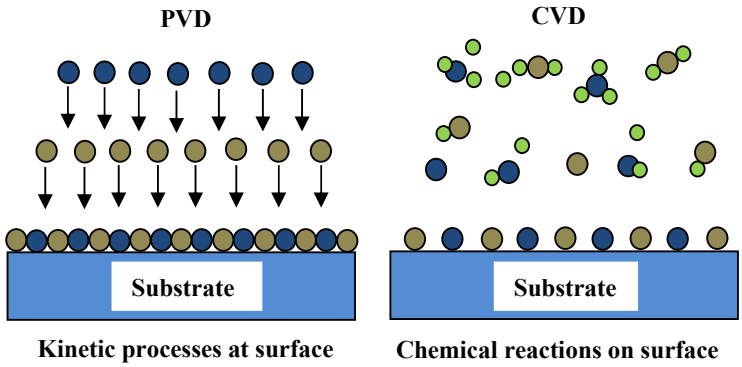

Fig. 1 The differences of the chemical and physical deposition techniques.

Almost all these deposition methods are actually used to manufacture gas sensors though many of these techniques are expensive and it will raise the prices of sensors. In manufacturing of thick and thin film sensors are mainly used Electro-deposition, Chemical bath deposition, Electro less deposition, Sol-gel/ Spray-pyrolysis and Ultrasonic techniques in Liquid phase deposition group and Glow discharge DC sputtering, Triode sputtering, Getter sputtering, Radio frequency sputtering (Magnetron and ion beam sputtering) and A.C. Sputtering in Sputtering

group (Table 1). In special cases Laser evaporation as well as Arc and R.E. Heating are also used in gas sensors manufacturing [14-17].

Before the discussion the applications of magnetron sputtering technology in manufacturing of gas sensors, it will be briefly described the characteristics of magnetron sputtering and the basic types of magnetron sputtering system used not only in gas sensors production but also for obtaining thin films for various proposes.

3. Magnetron sputtering

Magnetron sputtering is one of the best methods for obtaining thin films from very wide range of materials including metals, dielectrics, ceramics, polymers and so on. There are many types of magnetron sputtering methods that are the result of the development of this technology. The first magnetron sputtering experiments were published in the late 1930s, then a parallel-plate magnetron structure was presented in a patent and parallel capacitive-coupled RF sputtering systems were developed in 1962. The rotatable magnetron was created in the early 1980s, and tunable "unbalanced" magnetron sputtering was developed 12 years later. During the 1990s two advanced form of magnetron sputtering were introduced: ionized-magnetron sputtering and high-power impulse magnetron sputtering [18, 19].

3.1. The characteristics of magnetron sputtering

As mentioned above sputtering is a process whereby atoms of a solid target material are ejected (or vaporized) due to the momentum transfer from an atomic-sized energetic bombarding particle impinging on the target surface. Then these vaporized particles are condensed on the substrate material. The sputtering is carried out using gaseous ions from plasma that are then accelerated and directed toward the target. The plasma used during the sputtering is created and controlled by magnetron guns [20].

As known, plasma is weakly ionized quasi-neutral gas made up of ions and electrons to be a good electrical conductor. Generally, processes that depend on the use of the plasma are referred to as plasma processing. The plasma processing has plasma densities between $10^8 \sim 10^{13} / cm^3$ but in magnetically confined plasma (magnetrons) the plasma densities can be up to $10^{15} / cm^3$. The gas atoms may not be fully ionized and there are not only electrons and ions but also neutrals. The electron velocities are much higher than that of ions and neutrals. The plasma properties are heavily dependent on the excitation and ionization energies of the gas. The main plasma gases with their excitation and ionization energies are presented in Table 2 [21]. The most suitable gas is argon (Ar) because it is an 'inert' or 'noble' gas, thus not explosive when subjected to the RF $(13.56MHz)$ magnetic field or spark and it has low ionization energy $(15.7eV)$. The krypton gas is also a good candidate for this application, but it's expensive. Argon is relatively cheap to manufacture since it is extracted directly from the atmosphere [22-24].

Table 2. The main plasma gases with their excitation and ionization energies.

Gas	Excitation Energy (eV)	Ionization Energy (eV)	Ionization process
H_2	7.0	15.37-46	$H_2 \rightarrow H_2^+ + e^-$
H	-	13.6	$H \rightarrow H^+$
N_2	6.3	15.57, 24.5	$N_2 \rightarrow N_2^+ + e^-$
O_2	7.9	12.5, 20	$O_2 \rightarrow O_2^+ + e^-$
Ar	11.7	15.7	$Ar \rightarrow Ar^+ + e^-$
Kr	10	13.9	$Kr \rightarrow Kr^+ + e^-$
He	21.2	24.5	$He \rightarrow He^+ + e^-$
CO	6.2	14.1-44	$CO \rightarrow CO^+ + e^-$
CO_2	3.0	14-28.3	$CO_2 \rightarrow CO_2^+ + e^-$
NO	5.4	9.5-22	$NO \rightarrow NO^+ + e^-$
NO_2	-	11, 17.7	$NO_2 \rightarrow NO_2^+ + e^-$
N_2O	-	12.9-21.4	$N_2O \rightarrow N_2O^+ + e^-$
H_2O	7.6	12.59-19.2	$H_2O \rightarrow H_2O^+ + e^-$

Plasma can be used for different purposes depending on the type of the PVD process. It can be used as a source of ions or as a source of electrons. For applying power sources for discharge there are two sources: DC (continuous DC, Pulsed DC) and AC (LF $(\sim 100Hz)$, MF $(\sim 100 - \sim 1MHz)$ and RF $(> \sim 1MHz)$). For magnetron DC and AC sputtering processes plasma is used as a source of ions for the sputtering of material from a target material if the plasma ions are directed toward it. The uniformity of plasma is very important concern for more tunable deposition process environment. Plasma uniformity is mainly dependent on sputtering system geometry and the means by which the plasma was produced. The plasma produced by DC diode is not ideal for sputtering because the electrons ejected from the cathode are accelerated away from the cathode and are not efficiently used for sustaining the discharge [25, 26]. The more suitable sputtering structure for obtaining thin films is balanced magnetron system. This means, that besides the properties of plasma, the type of magnetron gun is also of great importance. In magnetron plasma configurations magnetic and electric fields are used to focus the plasma to the surface of the cathode-target. The cathode-target acts as the negative terminal and it provides an electron emitting surface. The electrons emitted from the cathode are mainly normal to the magnetic field lines and due to the Lorentz force, these electrons will then spiral around the magnetic field lines (Fig.2). The E/B 'magnetron' drift velocity is perpendicular to both the electric and magnetic fields [27-30]. The high flux of electrons generates high density plasma due to electron-atom collisions (high level of ionization). The positive gas ions created in the high density plasma are accelerated to the cathode-target due to the potential difference. The accelerated ions hit the target material and tear off small particles of target material. As higher the plasma density as higher the sputtering rate [31, 32].

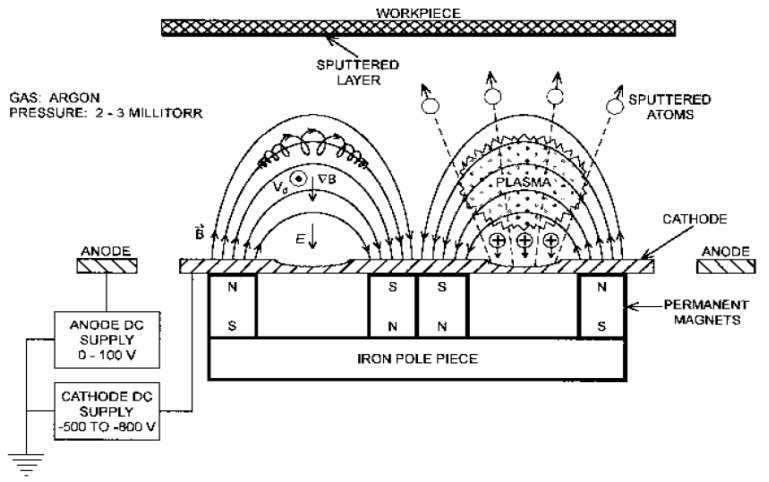

Fig. 2 Planar magnetron configuration [30].

Almost all tape of solid materials can be used as a target material for magnetron sputtering. The target materials used by magnetron sputtering obtaining thin films are presented in Table 3 [33-35].

The applying of DC potential is more convenient for conductor targets (metals) because there is no charge buildup for conducting targets otherwise a radio frequency (RF) potential may be applied instead of DC potential. The applying of RF potential, with a large peak-to-peak voltage, an alternating positive/negative potential appears on the target surface. The first part of each half-cycle the plasma ions are accelerated to the surface with sufficient energy to start sputtering and on the next half-cycles the ions move in the opposite direction to prevent any charge buildup. The prevention of charge build-up on the target material does not allow charging positively the surface of the target which will lead to stop the sputtering process. The RF sputtering also reduces the working pressure (increase plasma density for a given working pressure) [36-39].

Table 3. The target materials used by magnetron sputtering.

Type of material	**Element or compound**
Metals	Cu, Ti, Al, W, Mo, Cr, Si etc.
Oxides	ITO, $A1_2O_3$, In_2O_3, SnO_2, SiO_2, Ta_2O_5 etc.
Nitrides	TaN, TiN, AlN, Si_3N_4, CN_X
Carbides	TiC, WC, SiC
Sulfides	CdS, CuS, ZnS
Oxycarbides and oxynitrides of Ti, Ta, Al and Si	

All mentioned PVD processes are conducted in a vacuum or low pressure gaseous environment and the parameters of sputtering process as well as the properties of the growing film largely depend on the vacuum properties. Generally, the vacuum system consists of a chamber, a pumping system and a gas injection system. The vacuum levels are divided into several ranges. The general ranges of pressure/vacuum are classified in Table 4. Depending on the sputtering type and the application field of growing films the different degree or quality of vacuum can be used [40-42].

Table 4. The general ranges of vacuum levels.

S.N	**Pressure/Vacuum**	**In Torrs**	**In SI unit**
1	Atmospheric pressure	760	101kPa
2	Low vacuum	760-25	100^{-3} kPa
3	Medium vacuum	25-$1x10^{-3}$	3 kPa-100 mPa
4	High vacuum	$1x10^{-3}$-$1x10^{-9}$	100 mPa-1 μPa
5	Ultra high vacuum	$1x10^{-9}$ -$1x10^{-12}$	100 nPa-100 pPa
6	Extremely high vacuum	< $1x10^{-12}$	< 100 pPa
7	Outer space	$1x10^{-6}$ -$3x10^{-17}$	100 μPa to < 100 fPa
8	Perfect vacuum	0	0 Pa

For the purposes of film fabrication using in gas sensor manufacturing it is meanly applied the medium vacuum range while the films used in military and space stations equipment requires a fairly high purity materials obtained in very high vacuum range. Despite all this, it is often more appropriate to use low or medium vacuum levels for different reasons. For example, a low pressure environment provides a long mean free path for collision between the original source of the material and the location upon which the particles are deposited. On the other hand, the vacuum environment allows for the control and decreasing of contaminants in a given system during film growth. The contaminant can affect the film properties or influence the film stability in an undesirable way. It is very important to know the reasons of contamination and it can be related to gaseous impurity, the cleanliness of the chamber material, debris and so on. Contamination is an unknown variable which can affect the reliability or the reproducibility of the deposition process [43, 44].

3.2. The configurations of magnetron system

There were various types of magnetron systems: planar balanced magnetron device, unbalanced magnetron device, closed-field unbalanced magnetron device, pulsed magnetron device, variable field magnetron device and high power pulse magnetron device. In this section it will be briefly discussed the most applicable types of magnetron systems [45, 46].

The most common and simple magnetron configuration used in gas sensor manufacturing is the planar magnetron (Fig.2 and Fig. 3(a)) [47, 48]. For this system it can be used both the DC and RF potentials described above. Here the array of permanent magnets behind the cathode arranged in such a way as to create a region of magnetic field directly above the target. As mentioned above the magnetic field is oriented radially and directly above the cathode surface. So, the E X B drift path creates a circle along the target surface making a high plasma density environment along this path. Due to the no uniformity of the plasma on the target, a circular region known as the "racetrack" is created (Fig. 4) [49]. This is the reason why the target using efficiency is only 20% to 45%. The "racetrack" effect can be minimized to make rotation of the substrate and magnet, but this leads to time-varying deposition rates and incident angles and ultimately can affect the film properties [46, 50].

In the planar magnetron the plasma is mainly restrained to the target region. The region of dense plasma extends about $50-60mm$ from the target surface and there takes place the ion

bombardment. The ion bombardment and film growth processes affect each other which influence the structure and properties of the growing film. If the substrate is in the low plasma region (outside of dense plasma region) the ion current $(1 mA/cm^2)$ flowing to the substrate is not enough to affect on the film structure but here the ion bombardment energy is low. If the negative bias applied to the substrate the ion energy increases which can lead to create defects in the film. So it is not easy to deposit fully dense film by conventional planar magnetron [51].

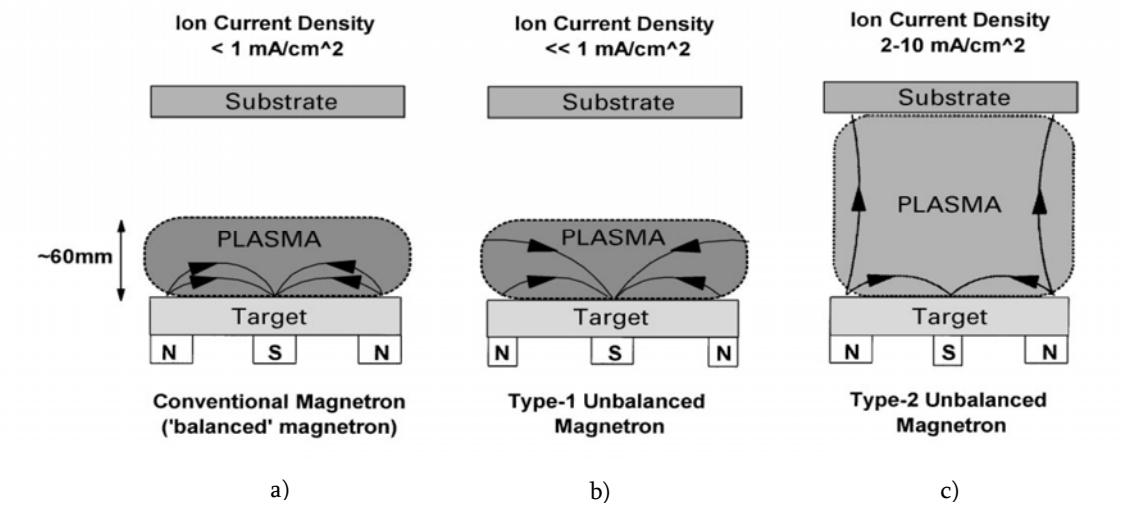

Fig. 3 The magnetron configurations [47].

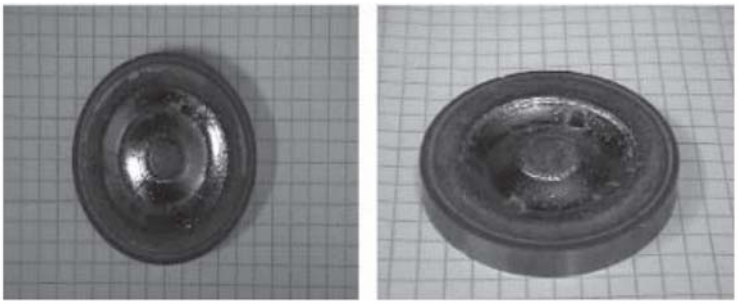

Fig. 4 The "racetrack" in a 2" circular Si planar magnetron sputtering target [49].

If it will be used a high flux $(> 2 mA/cm^2)$ ions with low energy $(100eV)$, the deposition process can carry out without intrinsic stresses. Those conditions can be realized by unbalanced magnetrons (Fig.3 b), c)). Generally, the term of "balanced" and "unbalanced" magnetrons related with ion bombardment. The "balanced" magnetron system has a low ion bombardment while in "unbalanced" arrays are generated higher ion bombardment. In order to determine the degree of unbalance, the magnetron arrays can be divided into 6 groups (Table 5) according to the value of **g**, which is equal to $\mathbf{Z_{Bz=0}/W_{1/2}}$, where **Z** is the distance to the null point and **W** is the target width (Fig. 5) [52].For the given magnetron design, **g** can vary within the interval $0.3 - 3.3$, depending on the current in the electromagnetic coil [53,54].

Table 5. The degree of unbalance for magnetron arrays.

Group Number	Group Description	$g=Z_{Bz=0}/W_{1/2}$
I	Extremely balanced	g≥2.00
II	Very balanced	1.75≤ g <2.00
III	Medium balanced	1.50≤ g <1.75
IV	Unbalanced	1.25≤ g <1.50
V	Very unbalanced	1.00≤ g <1.25
VI	Extremely unbalanced	g<1.00

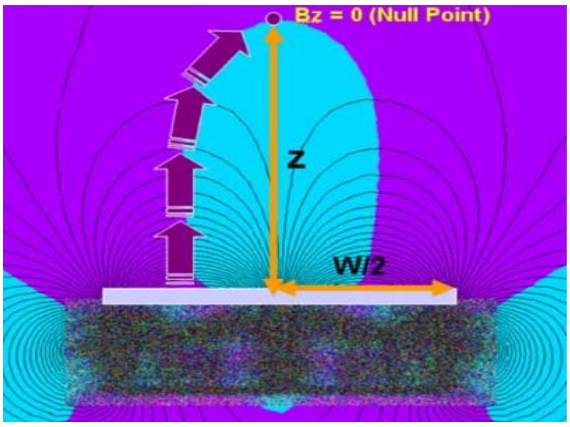

Fig. 5 Magnetic field lines of magnetron system [52].

In case of the balanced magnetron, the all magnetic field lines are closed and the electrons mainly accumulate the target. In unbalanced magnetron system the outer ring of magnets is strengthened compared to the middle part (pole). So, in this case there are some field lines those are not closed and directed towards the substrate. Due to the unclosed magnetic lines some electrons follow the tracks of the lines reaching to the substrate. This means that the plasma is not entirely focused on the target and can partly reach the substrate. In this way without applying an outer bias to the substrate a high ion currents can be extracted from the plasma. If we need a high deposition rate it is more preferable to use the "Type-2" system (see Fig. 3 c)) [49, 55].

4. Gas sensors manufactured by magnetron system

With the development of global industry and technology, the demand for different types of gas sensors is increasing year by year. Such sensors can be used in various fields, for example in security systems, in air quality control system, in technological process control and so on. Semiconductor gas sensors, as the most preferred gas sensor structure used in real life, must be accurate and high-speed, have high sensitivity and selectivity, low power consumption, and small dimensions. From this point of view, there are still many problems in this field and these parameters need to improve by changing the sensing materials, the doping degree in these materials, geometric dimensions of sensing system, the morphology of sensing layer, the grains and necks sizes of the active layer and so on [56-60].

4.1. Gas sensing materials

Magnetron sputtered metal oxides have been used for gas sensing not only in a single-component forms but also in multicomponent structures. These materials are typically non-organic substances with a variety of morphologies including dense thin and thick films, porous granular structures, nanowall, nanobelts, nanotubes and so on. The main single-component metal oxides used in conductametric gas sensors sensitive to both oxidizing and reducing gases are the following: $SnO_2, In_2O_3, ZnO, TiO_2, WO_3, Ga_2O_3, Fe_2O_3$, etc. Metal oxide composites and mixed metal oxides, which have shown increased sensitivity to various gases, are listed in Table 6 [61].

Table 6. The metal oxides composites and mixed metal oxides sensitive to various gases.

Metal oxide composites and mixed metal oxides	Target gases
$Cr_{2-x}Ti_xO_y$; SnO_2-Co_3O_4; SnO_2-Fe_2O_3; SnO_2-Mn_2O_3; SnO_2-MoO_3; SnO_2-ThO_2; In_2O_3-SnO_2; In_2O_3-Ga_2O_3; In_2O_3-Co_3O_4	CO
SnO_2-In_2O_3; SnO_2-CuO; SnO_2-ZnO; SnO_2-TiO_2; TiO_2-NiO; In_2O_3-ZnO; Zn_2O_3-Ga_2O_3	H_2
SnO_2-MoO_3; SnO_2-Fe_2O_3; SnO_2–SiO_2-AgO_y; SnO_2-RuO_x; ZnO-CuO; ZnO-RuO_2; ZnO-MnO_2; α-Fe_2O_3-ZnO; TiO_2-CuO; TiO_2-Cr_2O_3; Cr_2O_3- Fe_2O_3	NH_3
ZnO-Ga_2O_3; ZnO-SnO_2; ZnO-CdO; ZnO-Al_2O_3; In_2O_3-ZnO; In_2O_3-SnO_2; Fe_2O_3- SnO_2; SnO_2-Y_2O_3; SnO_2-NiO; SnO_2-Sb_2O_5; SnO_2-MoO_3; SnO_2-SrO; SnO_2-CaO; SnO_2-WO_3; WO_3-Bi_2O3; WO_3-In_2O_3; WO_3-TiO_2	NO_x
α-Fe_2O_3-SnO_2; α-Fe_2O_3-ZrO_2; α-Fe_2O_3-TiO_2; α-Fe_2O_3-In_2O_3; α-Fe_2O_3-CuO; In_2O_3-Ga_2O_3; In_2O_3-ZnO; In_2O_3-SnO_2; SnO_2-MoO_3; SnO_2–SiO_2; SnO_2-CeO_2; SnO_2-CuO; SnO_2-CdO: SnO_2–TiO_2; SnO_2-NiO; SnO_2-La_2O_3; SnO_2-ZnO; Co_3O_4-ZnO; TiO_2-CuO; WO_3-TiO_2	Ethanol
SnO_2-MoO_3; SnO_2-ZnO; SnO_2-In_2O_3; SnO_2-CuO; SnO_2-NiO; SnO_2-La_2O_3; SnO_2-Sm_2O_3; Fe_2O_3-SnO_2; α-Fe_2O_3-NiO; WO_3-SiO_2; Co_3O_4-ZnO; ZnO-CuO	VOCs
In_2O_3-Ga_2O_3; In_2O_3-SnO_2; In_2O_3-SnO_2-TiO_2; SnO_2-CaO; SnO_2-K_2O; $La_{1-x}Mg_xFeO_3$	CH_4
In_2O_3-Ga_2O_3; In_2O_3-Fe_2O_3; In_2O_3-CeO_2; In_2O_3-ZrO_2; In_2O_3-NiO; In_2O_3-ZnO-SnO_2; In_2O_3-SnO_2; SnO_2-CoO_x; SnO_2-Fe_2O_3; WO_3-CoO_x; ZnO-CdO	O_3
SnO_2-CuO; SnO_2-Ag_2O; ZnO-CuO; ZnO-TeO_2; WO_3-CuO; Fe_2O_3-SnO_2; TiO_2- Nb_2O_5; $BaSrSnTiO_3$-CuO; CdO–In_2O_3	H_2S
$BaTiO_3$-CuO-La_2O_3; CuO-$CuxFe_{3-x}O_4$; SnO_2-La_2O_3	CO_2
TiO_2-V_2O_5; V_2O_5-WO_3-TiO_2; WO_3-Ag_2O; SnO_2-NiO	SO_2
$W_{18}O_{49}$–SnO_2; $NiFe_2O_4$; $ZnFe_2O_4$; In_2O_3- Fe_2O_3	Cl_2

It was established that such metal oxide composites and mixed metal oxides nanocomposites with specific composition for given target gases were capable to increase the activities of many chemical reactions. As mentioned above when the sensitive material is chosen, it is very important to choose the right technology for thin film obtaining. If the technology is PVD based method, particularly any type of magnetron sputtering, then film properties will largely depend on technological process modes during sputtering. Changing the magnetron generator's power, the pressure of inert gas, the substrate temperature and the sputtering duration can be significantly influenced by the gas sensing properties of active layer [62-66].

4.2. Magnetron sputtered gas sensors

The sensitivity to different gases depends on the microstructure of the sensing material, especially on the porosity and grain size [67-70]. The morphologies of the $Cr_2O_3 : CuO$ $(50 : 50$ weight $\%)$ thin films deposited with the RF powers of 200 and $300W$ on FTO and Si substrates were illustrated [71]. As it is common for magnetron sputtering the grains formed for the films deposited at $200W$ RF power have significantly smaller dimensions than those of grains formed at $300W$ RF power (Fig.6). In the case of higher RF powers, the ions have more energy at the time of collision and the bombardment with higher energy leads to deposit larger nanocrystallites.

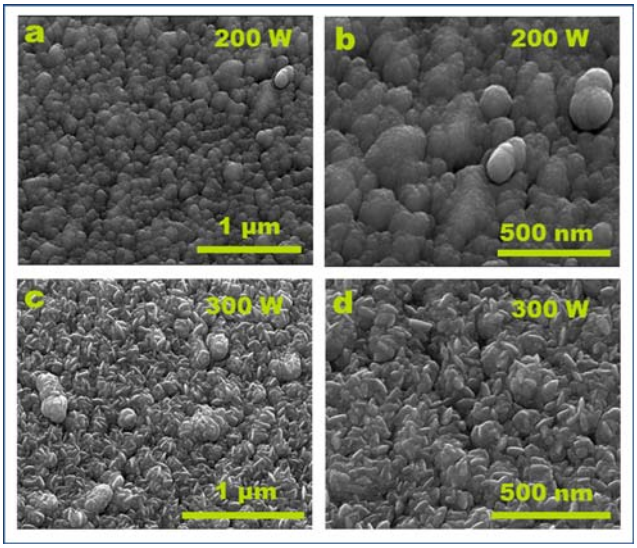

Fig. 6 The FESEM images of Cr_2O_3:CuO (50:50) thin films deposited with the RF powers of 200 and 300 W [71].

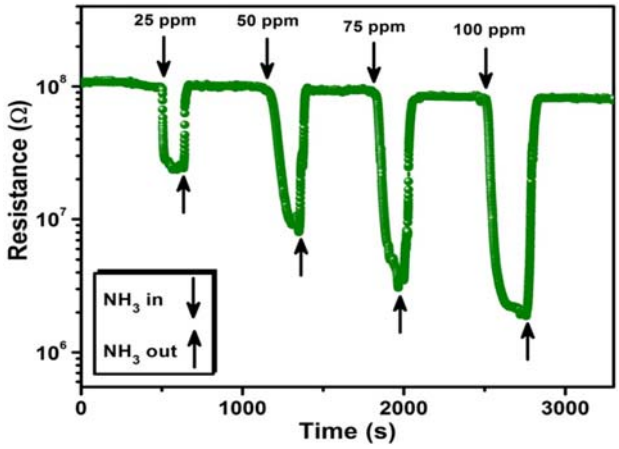

Fig. 7 The gas sensing response characteristics of Cr_2O_3:CuO (50:50) thin films deposited with 300W RF power for different concentration levels of NH_3 gas [71].

The deposited thin film with nanocrystallites had a good sensitivity to small concentration of NH_3 gas (Fig. 7).

The thin $In_2O_3 : G_2O_3$ films with nanoparticles were obtained by RF magnetron sputtering as a good material for LPG sensing (Fig. 8) [72]. By changing the sputtering duration and the power of magnetron generator the best sensitivity has been revealed. The variation of sputtering time allowed to obtain $In_2O_3 : G_2O_3$ films of different thicknesses with the RF constant powers of $60W$. The increase in the film thickness is followed by a monotonic decrease in the sensitivity. In case of most thin film the sensitivity to $5000\,ppm$ LPG was equal to 9 (Fig. 9 (a)).

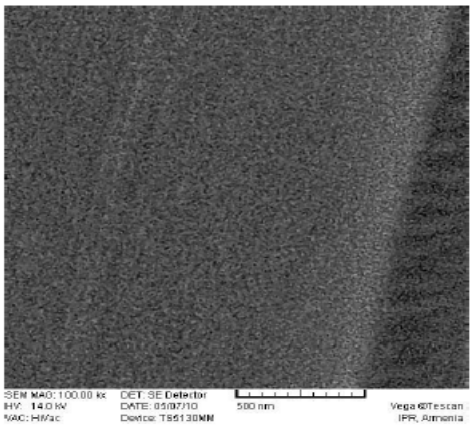

Fig. 8 The SEM image of In_2O_3:G_2O_3 (96:4 weight %) thin films deposited with the RF powers of 60 W [72].

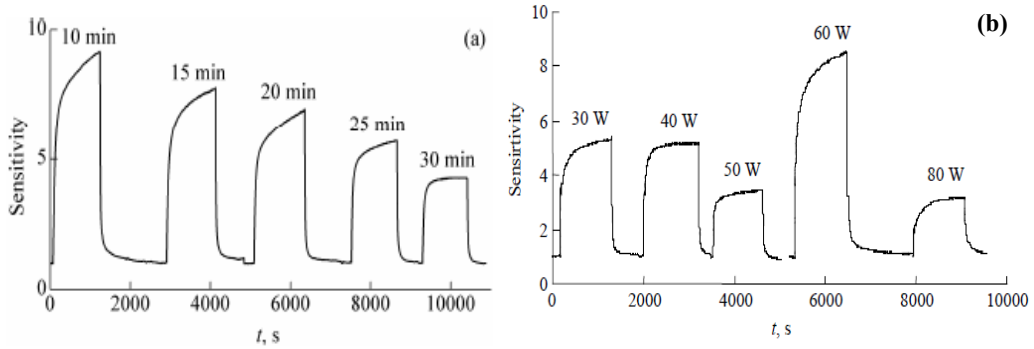

Fig. 9 (a) The sensitivity of gas sensors based on glass ceramics/In_2O_3:Ga_2O_3 (96:4 weight %)/Pd at the presence of 5000 ppm LPG obtained with the RF powers of 60 W and different sputtering duration, (b) the sensitivity of gas sensors based on glass ceramics/In_2O_3:Ga_2O_3 (96:4 weight %)/Pd structure at the presence of 5000 ppm LPG obtained during 15 min with the different powers of the magnetron generator [72].

The results of real time measurements of the sensitivity of sensors whose films were obtained with sputtering during 15 minutes at different powers of the magnetron generator are presented in Fig. 9 (b). The peak of sensitivity is observed for the sensitive film obtained at the RF power of $60W$. Since the change in the sputtering power leads, as mentioned above, to the change in both the thickness and grain size of films, it may be assumed that the peak of the sensor sensitivity is associated with the fact that in the film prepared at the power of $60W$ and the

sputtering time of 15 minutes such a combination of grain size and film thickness occurs for which both the diffusion of the influencing gas and its interaction with the film take place more intense than in other cases [73].

Magnetron sputtered thin films with different nanostructures had sensitivity to various gases such as ammonia, hydrogen sulfide, acetone, ethanol, methane, acetaldehyde, ethanol, NO_2, LPG, hydrogen peroxide, isobutene, NO_x and so on. Summary of the features and sensing properties reported for magnetron sputtered complex metal oxides are presented in Table 7. By magnetron sputtering techniques there were produced not only films with nanograins (nanoparticles), but also different structures such as nanowall, pyramidal-shape particles, heterojunction, nanoplates and so on, which improves these sensors' parameters and makes them more competitive and applicable.

Table 7. The features and sensing properties reported for magnetron sputtered complex metal oxides.

Sensing material	**Film structure**	**Type of magnetron**	**Detecting gas**	**Gas concentration (ppm)**	**Sensitivity**	**Ref.**
Cr_2O_3:CuO	nanoparticles	RF magnetron	ammonia	100	98%	[71]
ZnO<Cu>	nanoparticles	RF magnetron	hydrogen sulfide	5	65%	[74]
ZnO<Bb>	nanowall	RF magnetron	acetone, ethanol	100	85%	[75]
TiO_2	nanoparticles	RF magnetron	Methane	1000	95%	[76]
Indium–Tin Oxide	nanoparticles	DC reactive magnetron	acetaldehyde	10	40%	[77]
CuO	nanoparticles	RF reactive magnetron	ethanol	250	75%	[78]
$MgIn_2O_4$	nanoparticles	RF magnetron	ethanol	500	4	[79]
NiO	pyramidal-shape particles	RF reactive magnetron	hydrogen	1000	70%	[80]
SnO-SnO_2	heterojunction	RF reactive magnetron	NO_2	10	4.35	[81]
ZnO<Ni >	nanoplates	RF magnetron	hydrogen	5	18%	[82]
In_2O_3:G_2O_3	nanoparticles	RF magnetron	LPG	5000	8	[72]
SnO_2<Co>	nanoparticles	RF magnetron	hydrogen peroxide	105	290	[83]
SnO_2/MWCNT	nanoparticles	RF magnetron	isobutane	5000	50	[84]
In_2O_3-SnO_2	nanoparticles	RF magnetron	NO_x	50	5	[85]

Here the dominant part of manufactured sensors obtained by RF magnetron sputtering methods and mainly the films had granular structure (nanoparticles). Magnetron sputtering allows easy control of grain size and thickness of the sensing layers which greatly affect the sensors parameters.

5. Conclusions

Physical vapor deposition has been used for obtaining of a wide variety of gas sensitive metal oxides. Particularly, magnetron sputtering gives an opportunity to manipulate deposition conditions, to alter microstructure and promote formation of nanostructured materials. This method allows deposit thin and thick layers almost any kind of target materials sensitive to both oxidizing and reducing gases. Magnetron sputtering has emerged to complement other vacuum coating techniques due to the many advantages such as high deposition rates, ease of sputtering any metal, alloy or compound, high-purity films, extremely high adhesion of films, ability to coat heat-sensitive substrates, ease of automation and excellent uniformity on large-area substrates. All of these advantages allow us to say that this technology is one of the best technologies to produce gas sensors and in the near future it will develop more and more related to the increasing demand in gas sensors with high sensitivity, selectivity and stability.

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