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Sputtering of Thin Films

Napr̆ševanje tankih plasti

J. Musil[1], Institute of Physics, Prague

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The sputtering and evaporation of solid materials are fundamental physical processes now currently used in the Physical Vapour Deposition (PVD) of thin films. Up to the mid 70 s, however, evaporation dominated over sputtering in PVD technologies. It was due mainly to a very low sputter deposition rate of the film and relatively high pressures (> 1 Pa) needed to sustain the sputtering discharge. The breakthrough arrived when the planar magnetron was discovered by Chaplin[1] in 1974. From this moment a very strong development of the sputtering method started. In this paper the main milestones reached in the development of sputtering discharges and deposition of thin films are given. Also, the present trends of the next developments in this field which will meet the requirements of new advanced technologies in the first years of the 21st century are outlinned.

Key words: sputtering, evaporation, phyşical vapour deposition, thin films, magnetron, plasma

Naprševanje in izparevanje trdih snovi sta fizikalna procesa, ki sta osnova današnjih fizikalnih (vakuumskih) postopkov nanašanja (PVD) tankih plasti. Do sredine sedemdestih let je naparevanje prevladovalo v PVD tehnologijah. To pa v glavnem zaradi majhne hitrosti nanašanja in relativno visokega tlaka (> 1 Pa), ki je bil potreben pri naprševanju za vzdževanje plazme. Do preloma je prišlo leta 1971, ko je Chaplin razvil magnetron. Od takrat naprej je bil razvoj postopkov naprševanja zelo intenziven. V tem prispevku so podani glavni mejniki pri razvoju le-teh. Osvetlili bomo tudi sedanje trende razvoja na tem področju v luči zahtev sodobnih tehnologij za 21 stoletje.

Ključne besede: naprševanje, naparevanje, fizikalni (vakuumski) postopki nanašanja, tanke plasti, magnetron, plazma

1 Milestones in sputtering

1.1 Diode sputtering

In diode sputtering the substrate is fully immersed into a plasma and the substrate is placed on an anode. Therefore, the substrate is exposed to a flux of electrons which are incident on it. The diode discharge is sustained at high pressures (> 1 Pa) at high discharges voltages ranging from about 1 kV to 5 kV. The ionization of the sputtering gas is low and so the deposition rate of the film is also very low (<< 0,1 μm/min). The deposition rate of sputtered films is considerably lower than that of evaporated films. This was the main reason why diode sputtering was not utilized in industrial fabrication of thin films.

1.2 Magnetron sputtering

In magnetron sputtering a magnetic field is used to sustain the sputtering discharge in the close vicinity of a sputtered cathode (target). The magnetic circuit placed behind the sputtered cathode forms above it a tunnel of semitoroidal magnetic field B. In this closed B field tunnel the plasma is confined and due to the drift of electrons along the tunnel axis in crossed E and B fields the sputtering gas is very efficiently ionized. This system is called the conventional magnetron (CM). High plasma density near the target surface results in a decrease of plasma impedance and so in a decrease of the discharge voltage down to about 500 V and mainly in a dramatic increase of the deposition rate of the film up to about 1 μm/min. This sputter deposition rate is already sufficiently large enough to be competitive with the deposition rate of evaporated films. The high deposition rate, simple design and so very reliable magnetron cathode were the main reasons for the extremely rapid introduction of the magnetron technology into industry.

1.3 Unbalanced magnetron

Due to the efficient plasma confinement near the magnetron target the substrate lies in a weak plasma or even outside of it. From the plasma only small ion currents can be extracted and the substrate ion current densities i_s are small, below 1 mA/cm^2. Low i_s are, however, insufficient to control the microstructure of the growing film and to produce dense, compact films. To produce such films i_s greater than 1 mA/cm^2 are required. This can be achieved in an unbalanced magnetron (UM) where an external magnet is added to the magnetic circuit of the CM[2]. The polarity of the external magnet is reversed to that of the internal one. It improves the plasma confinement above the target surface, increases the plasma density and also ensures the trasport of the plasma from the target to the substrate where $i_s > 1$ mA/cm^2 can be easily achieved. Under these conditions the ratio of ion and coating material fluxes, incident on the substrate, is greater than 1. It means that the UM sputtering system is fully equivalent to ion plating systems based on evaporation.

1.4 Low pressure sputtering

The main problem in sputtering at low pressures is to eliminate losses of charged particles from the sputtering discharge. This can be achieved by improving the plasma

[1] Prof. Jindrich MUSIL
Institute of Physics
Academy of Sciences of the Czech Republic
Na Slovance 2, 180 40 Prague 8, Czech Republic

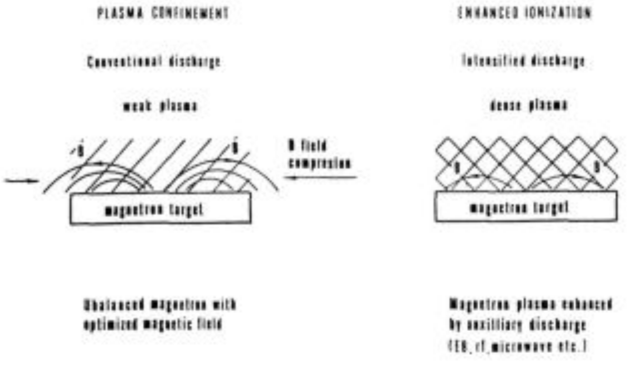

Figure 1: Basic principles of generation of low-pressure sputtering discharge

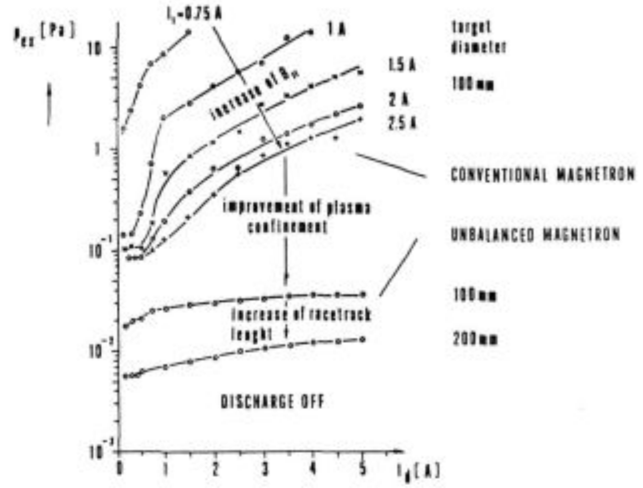

Figure 2: Effect of magnitude and shape of magnetic field and length of magnetron racetrack on pressure p_{ex} at which sputtering discharge extinguishes

confinement and/or by additional ionization of the sputtering gas. Principles of both methods are schematically shown in **Figure 1**.

The plasma confinement can be controlled by the shape of the magnetic field in the sputter deposition device. Typical examples of such sputtering systems are the magnetron using a multipolar magnetic field plasma confinement[3] and the two target magetron sputtering with electric mirrors[4,5]. The most efficient way to decrease the sputtering pressure is, however, to prevent the magnetic field lines to go beyond the edge of the target, see **Figure 1a**. This can be done by optimizing the magnetic field distribution above the magnetron target. Recently, it was achieved in new advanced UMs where the optimization of B-field distribution was performed by electromagnets and/or permanent magnets[6]. These low pressure UMs can operate down to 10^{-2} Pa with quite large discharge currents ranging from 0,1 A to several amperes. These magnetrons enable the realization of new technological processes where a collisionless, line-of-sight deposition is needed, for instance, for submicron integrated circuits metallization.

The plasma confinement in the magnetron sputtering discharge is controlled by the magitude and shape of the magnetic field B above the sputtered target. It clearly demonstrate experiments results of which are given in **Figure 2**. The sputtering pressure of CM decreases with increasing B to a certain limit which can be overcome only by a new qualitative improvement in the plasma confinement. This is realized by UM's. The UM's have also a limit in the minimum sputtering pressure p_{min} given by an optimum B-field distribution above the sputtered target. A further decrease of p_{min} can be achieved by a prolongation of the magnetron racetrack, see **Figure 2**. It is, however, a result of improved sputtering gas ionization.

The additional gas ionization results in an intensified magnetron discharge. It can be achieved, for instance, using a hot cathode electron emission[7], a hollow cathode electron source[8], and inductively coupled rf plasma[9,10] or a microwave plasma[11,12]. It is necessary to note that the additional ioization not only increases the degree of sputtering gas ionization but also results in the ionization of sputtered particles. It means that the additional ionization can also be used for the efficient production of metal ions at higher pressures ranging from several 0,1 Pa to several Pa[10].

1.5 Pulsed magnetron sputtering

Besides metal and alloy films also compound films, such as nitrides, oxides, borides, silicides etc, need to be deposited. The compound films can be prepared by reactive d.c. sputtering of metallic targets in a mixture of argon and reactive gas (O_2, N_2 etc). In this case the reactive gas incorporates in both the film and the sputtered target and causes so called target poisoning. This poisoning results not only in a significant decrease of the deposition rate but also in a charge accumulation on the target surface in the case when a dielectric film (e.g. Al_2O_3) is created on it. Charges accumulated on the insulating layers result in many unipolar arcs (sometimes called microarcs) which burn between different sites on the cathode, causing undesirable defects in the film and in the instability of the process. Recently, it was shown that these very serious limitations of d.c. reactive sputtering can be overcome using a magnetron fed by pulsed power[13]. During the pulse-on time the material is sputtered from the target and the insulating layer is formed on its surface, during the pulse-off time a discharging of the insulating layers through the plasma takes place. This periodic polarity changing prevents the generation of arcs and ensures good process stability. The pulsed magnetron sputtering (PMS) makes it possible to deposit good-quality insulating films and poorly conducting films in a stable process free from arcing. Also, a combination of the PMS with pulsed bias sputtering opens new possibilities in the production of films with the required microstructure under extreme conditions, for instance at low deposition temperatures.

2 Sputter deposition of thin films

It is well known that the film properties are determined by its microstructure, phase and chemical composition. What is the microstructure of deposited film it depends on parameters of the deposition process under which the film is created. Therefore, inter-relationships between process parameters, the film microstructure and its properties are intensively studied in many laboratories.

An understanding of these inter-relationships is very important for:

1. the reproducible production of films with prescribed properties
2. the development of new materials and technological processes.

2.1 Film microstructure

The film microstructure can be described by a structural zone model (SZM). SZMs display the film microstructure (M) as a function of different deposition parameters, e.g. $M = f(T/T_m)$, $M = (T/T_m, p_{Ar})$, $M = f(T/T_m, U_s)$, $M = f(T/T_m, E_p)$, where T and T_m are the deposition and melting temperature, respectively, p_{Ar} is the pressure of argon, U_s is the substrate bias, E_p is the energy delivered to the growing film per deposited particle.

The microstructure of the film can be divided into four zones, see **Figure 3**.

a) zone 1 - tapered crystallites separated by voids
b) zone T - densely packed fibrous grains
c) zone 2 - columnar densely packed grains
d) zone 3 - recrystallized grain structure

Main parameters which decide about the film microstructure are mainly the ratio T/T_m and the energy E_p. It is necessary to note that the energy delivered to the growing film by conventional heating (T/T_m) and particle bombardment E_p (atomic scale heating) are not physically equivalent (1 eV = 11600 K). It is one of main reasons of creation of different film microstructures under particle bombardment. Very important is also the kind of bombarding particles and their energy distributions.

2.2 Sputter deposition process

The film microstructure, phase and chemical composition can be controlled by two fundamentall processes:

1. Particle bombardment of growing film
2. "Mixing effect", i.e. an incorporation of additional elements into a base material.

The kind of particles which bombard the growing film varies with gas pressure and the energy E_p can be controlled either by the substrate bias U_s in the case of ion bombardment or by gas pressure p in the case of fast neutrals bombardment or by a combined action of both U_s and p. The particle bombardment can be classified as follows:

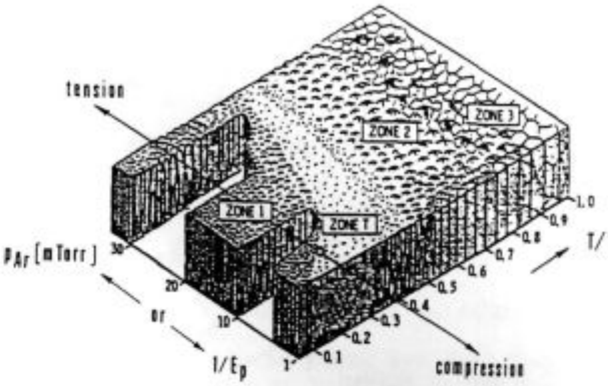

Figure 3: Structural zone model developed by J. A. Thornton for sputtered metallic films (after ref.[14])

1. Inert gas ions Ar^+ at $p > 0,1$ Pa, i.e. conventional sputtering when $\lambda < d_{s-t}$
2. Combined action or Ar^+ and fast neutrals at p ranging from 10^{-2} to 10^{-1} Pa, i.e. low pressure sputtering when $\lambda > d_{s-t}$
3. Ions of sputtered material M^+ at $p = 0$, i.e. self-sputtering when $\lambda >> d_{s-t}$.

Here, λ is the mean free path of particles and d_{s-t} is the target-substrate distance.

2.3 Ion bombardment of growing film

The energy of ions E_i bombarding the growing film can vary in a very wide range from eV to MeV. According to the magnitude of E_i we distinguish two basic processes:

1. Magnetron Sputter Ion Plating (MSIP) process which is based on low-energy ion bombardment (E_i from eV to about 1000 eV)
2. Ion implantation which uses a high-energy bombardment ($E_i >> 1$ keV) for the film modification.

Because in a sputter deposition of thin films the low-energy bombardment is used we will further analyse the MSIP process only.

2.3.1 Effect of low-energy ion bombardment on film microstructure

The effect of ion bombardment is determined by the energy per deposited atom E_p defined, in the simplest case of nonreactive deposition, as[15]:

$$E_p = E_i\, v_i/v_m = e(U_p - U_s)\, v_i/v_m \propto eU_s i_s/a_D \quad (1)$$

where E_i is the energy of ions, v_i and v_m are fluxes of ions bombarding the growing film and coating particles, respectively, U_p is the plasma potential, U_s is the substrate bias, i_s is the substrate ion current density, a_D is the deposition rate and e is the elementary charge.

The same value of E_p, however, does not correspond to the same microstructure of the film. According to Eq. (1) the same value of E_p can be achieved at different combinations of E_i and v_i/v_m when different physical

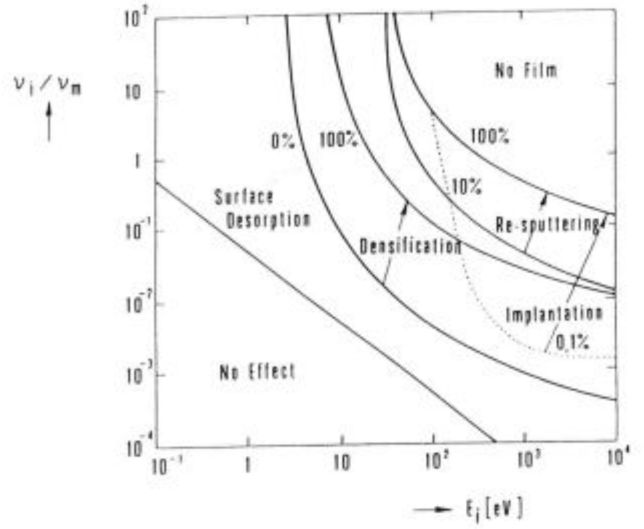

Figure 4: Schematic illustration of various ion bombardment processes as a function of E_i and v_i/v_m (after ref.[16])

processes can domiate, see **Figure 4**. Therefore, it is necessary to note that the parameters E_i and v_i/v_m are not physically equivalent.

For TiN films it was found that there is a critical values of $E_p = E_c$[17]. The films produced at $E_p < E_c$ are porous, soft, have a matt appearance and are in tension. On the contrary, films produced at $E_p > E_c$ are compact, dense, have a smooth surface, exhibit high reflection and are in compression. Films produced at $E_p = E_c$ exhibit zero stress. Every sputtered material can be characterized by a certain critical value $E_p = E_c$.

2.4 Mixing effect and formation of alloy films

A very important role in magnetron sputtering of thin films is played by the so called "mixing" effect, i.e. the addition of one or several elements to a base one element film. The amount and type of the additional elements can be used to control the size of grains in the sputtered film and to form nanocrystalline and amorphous films and also to form high-temperature structures at temperatures below 100°C. For more details see ref.[18,19].

3 High-rate magnetron sputtering and self-sputtering

In the past few years, attention begun to focus on high-rate sputtering due its new technological potential. There are three reasons why to develop this type of sputtering.

1. The possibility to shorten the film formation time, which makes an industrial coating production cheaper annd to replace ecologically damaging galvanic coating processes
2. The ionization of sputter material

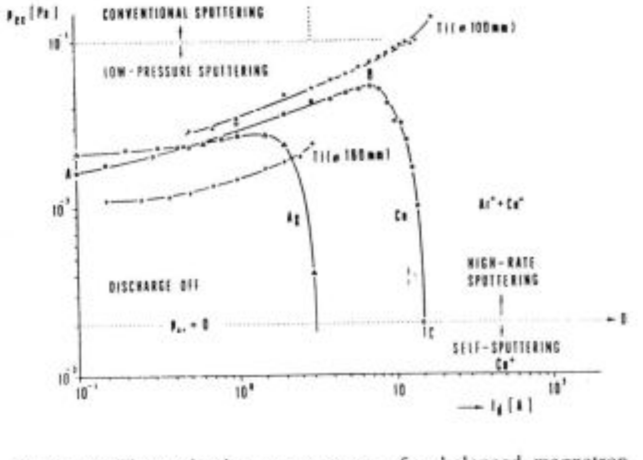

Figure 5: The extinction pressure p_{ex} of unbalanced magnetron discharge as a function of discharge current I_d for magnetron cathode of dia. 100 mm made of Cu, Ag and Ti[20]

3. The elimination of inert sputtering gas from the deposition process.

High-rate sputtering in absence of the inert sputtering gas is called self-sputtering. The ionization of sputtered material and/or elimination of the inert gas strongly influences the mechanism of film growth and increases the chemical reactivity in the formation of alloy and compound films.

4 Classification of magnetron sputtering

According to the sputtering pressure and the target power density $W_t = P_d/S$, the magnetron sputtering can be divided into four groups, see **Table 1**. This classification is based on measurements of an extinction pressure p_{ex} of the magnetron discharge generated by unbalanced dc magnetron with Cu target of diameter 100 mm as a function of the discharge current I_d, see **Figure 5**.

5 Present trends in sputtering development

The present trends in sputtering are strongly dictated by the urgent need for the development of new advanced materials and technological processes for their fabrication, which will meet the high requirements for the further development of human being in the first years of the 21st century. Three main directions have to be considered:

1. submicron microelectronics

Table 1: Classification of magnetron sputtering

Type of sputtering	p(Pa)	W_t(Wcm^{-2})
Conventional	> 0,1	< 30
Low-pressure	< 0,1	< 50
High-pressure	> p_o	> 50
Self-sputtering	0	> 50

p_o is the base pressure

2. surface engineering
3. biomaterials with strongly enhanced surface properties.

To master high density submicron microelectronics (down to 0,1 μm) it is necessary to develop highly electrically conductive and highly insulating films, efficient barrier films, multilayered structures made of ferromagnetic materials and multilevel metallization including perfect trench coatings. For this purpose low pressure (< 10^{-1} Pa) sputtering, self-sputtering ($p_{Ar} = 0$) and homogeneous large area (up to 400 mm diameter of Si wafer) deposition have to be developed.

The main task in surface engineering will be first of all to replace ecologically damaging wet galvanic processes, particularly hard chromium, by dry PVD processes. A very promising candidate to do this is the high-rate and self-sputtering processes. Considerable attention will be devoted to the formation of a diffused interface which ensures a good bonding of the coating to the substrate. The key role in the solution of this problem will be played by sputtered amorphous and/or nanocrystalline alloy films which will support the interdiffusion of the substrate and coating elements and enhance the surface functional properties of the coating.

Biomaterials will need more sophisticated coatings which will meet strong requirements of compatibility with the human tissues and blood. Also here the sputtering is expected to be an efficient method for the production of films with controlled microstructure, texture, permeability or films exhibiting strong barrier effects, for instance highly adhesive, wear resistant films on implants or polymer films filled by metal clusters.

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6 References

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