Fabrication of Al_2O_3 and AlN thin films by reactive sputtering and its optimization using DOE

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Abstract

Thin films of Al_2O_3 and AlN have been fabricated by reactive sputtering at a magnetron sputtering equipment. Mixture of Ar and O_2 has been used for fabrication of Al_2O_3 films, mixture of Ar and N_2 has been used for fabrication of AlN films. Optimization of the fabrication process has been carried out using DOE (Design of Experiments). Experiments of the type 2^3 have been used for creating of mathematical models of sputtering processes. The results calculated of the models have been compared with the results obtained at the fabrication process. It has been found very good coincidence among the results calculated of mathematical model and measured on fabricated layers.

Keywords: thin films, PVD, magnetron sputtering, reactive sputtering, Al_2O_3 thin films, AlN thin films.

Introduction

There are many different types of sputtering processes [1], [2]. The basic classification is carried out according to the voltage used for powering of glow discharge inside the recipient: DC or AC type. The DC process is usable for sputtering of conductive films only; the AC process can be used for fabrication of conductive as well as insulating films. The process can be carried out in diode or triode arrangement and as reactive or non-reactive sputtering.

Reactive deposition is widely used to fabricate thin dielectric films, which have the required properties and be produced on substrate materials such as alumina and glass [3]. Considerable progress has been achieved in developing enhanced and intensified plasma-assisted PVD to decrease the processing pressure. To support a glow discharge at low pressures (0.5-10 Pa) it is necessary to increase the electron path or to provide additional electrons. The later case can be also obtained by using a triode arrangement generally of a positive electrode and a thermionic source in addition to the conventional diode system. The electrons produced are then attracted by the positively charged bias electrode and increase ionization in plasma [9]. The working gases consist of argon and reactive species. The object of the process is to create films of closely controlled stoichiometry. The rate and composition of the sputtered atoms together with the reaction kinetics of the surface reaction on the substrate is important in the deposition process.

If a sputtering process is of a DC type, the target is joined with negative potential [6], [7]. Positive ions of the gas are accelerated toward to the target. Bombardment of the target by these ions causes emission of atoms of the target together with secondary electrons, which increase ionization of gas.

If magnetron sputtering is used a strong magnetic field is applied for modification of movements of electrons. The paths of the electrons are modified toward to a spiral and a sputtering yield of the electron increases. The number of atoms ionized by one electron increases too, and the sputtering process is more intensive.

Increase of ionization efficiency of the electrons makes also ignitions of a glow discharge at lower pressure possible. The lower is the pressure of the gas inside the recipient during sputtering process, the lower number of molecules of the gas is inbuilt inside the fabricated thin film, and density as well as quality of the film increase.

Quality of the sputtered film is strongly influenced by the quality of the surface of the substrate [4], [8]. With the respect to the thickness of fabricated films, usually from 30 nm to 1 μm, the film follows defects of the surface of the substrate.

After sputtering the film are very often stabilized. Stabilization is realized by curing of the films at the higher temperature, usually from 120°C to 200°C for 30 to 60 minutes.

Optimization of the sputtering process is not a simply problem [5]. Therefore a method of factorial experiments has been used to find a mathematical model, which would describe a process with sufficient accuracy.

1. Theory

1.1 Reactive sputtering

The principle of reactive sputtering is shown in Fig. 1.

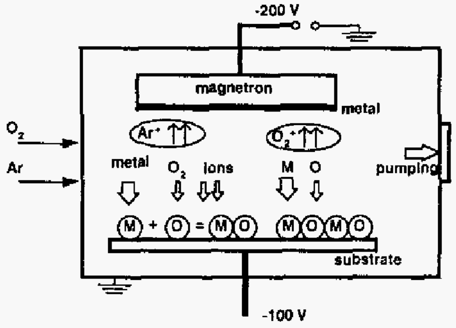

Fig. 1 Principle of reactive sputtering of MO layers (M ... metal, O ... oxygen). If oxygen is substituted by nitrogen, MN layers are fabricated

The target is bombarded by Ar and O atoms. The surface consists of target $c1$ and oxygen (or nitrogen) c_2 atoms, where c_1 and c_2 are relative surface concentrations ($c_1 + c_2 = 1$). The sputtering rate of i-type atoms let us define as the frequency probability of the removal of i-type atoms $w_i = Y_i\, i_0$, where Y_i is the sputtering yield of i-type atoms and i_0 is the normalized ion irradiation intensity ($i_0 = I_0/C$, where I_0 is the flux of arriving ions and C is the surface concentration of atoms). The adsorption rate of i-type atoms to the j-type atoms on the surface is defined as κ_{ij}, which can be expressed by the equation

$$\kappa_{ij} = \frac{\alpha_{ij}^{(T)}}{C}\frac{p_i}{\sqrt{2\pi mkT}} = \alpha'_{ij} p_i \tag{1}$$

Where αij ... the sticking coefficient of i-type atoms to j-type atoms.

The kinetics of the surface concentration of target material atoms in the presence of sputtering and oxygen adsorption is obtained as the solution of the following equation

$$\frac{dc_1^{(T)}}{dt} = w_2 - (w_2 + \kappa_T)c_1^{(T)} \tag{2}$$

Let us denote the target material atoms by index 1 and oxygen atoms by index 2. Resputtering processes are neglected.

$$\kappa_{11}^{(T)} = \kappa_{12}^{(T)} = 0 \tag{3}$$

The sticking probability of oxygen atoms on the top of atoms of the target is assumed to be equal to zero.

$$\kappa_{22}^{(T)} = 0 \tag{4}$$

It makes that the target oxidation reactions are defined by one flux of oxygen atoms.

$$\kappa_{21}^{(T)} = \kappa_T \tag{5}$$

which is equal to Eq. (1)

The kinetics of the surface concentration can be expressed using the equation

$$\frac{dc_1^{(T)}}{dt} = w_2 - (w_2 + \kappa_T)c_1^{(T)} \tag{6}$$

The surface concentration of non-oxidized atoms exponentially approaches the steady state surface composition

$$c_1^{(T)} = w_2/(w_2 + \kappa_T), \quad c_2^{(T)} = \kappa_T/(w_2 + \kappa_T) \tag{7}$$

The characteristic approach time is equal to $1/(w2+\kappa T)$. The steady state sputtering rate $v_{sp}=\Sigma w_i c_i$ is equal to

$$v^{(T)} = w_2\left(\frac{w_1 + \kappa_T}{w_2 + \kappa_T}\right) \tag{8}$$

Equation (8) can be expressed as a function of the partial pressure of oxygen

$$\frac{v^{(T)}}{w_2} = \frac{(w_1/w_2) + (\alpha'/w_2)p}{1 + (\alpha'/w_2)p} \tag{9}$$

Fig. 2 shows the calculated dependences of the sputtering rate on the partial pressure of the reactive species in relative unites (w_2/α) for w_1/w_2 = 0.5; 1.0; 2.0; 3.0; 4.0; 5.0 and 6.0 (curves 1-6, respectively). It follows that with the increase of the partial pressure of oxygen the sputtering rate changes from the "metallic" mode to the "oxide" one.

Sputtering yield of the sputtering process is expressed using equation

$$Y = \frac{Na}{Ni} \tag{10}$$

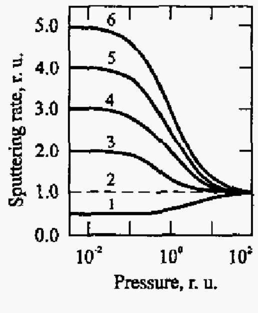

Fig. 2 Calculated sputtering rate vs. partial pressure of reactive species in relative unities w_2/α for different ratios w_1/w_2.

Where N_a … number of sputtered atoms, N_i … number of ions achieving the target.

If the ions bombard the target perpendicularly, the sputtering yield can be described by the equation

$$Y = \frac{3\alpha}{4\pi^2} \cdot \frac{4m_i m_t}{(m_i + m_t)^2} \cdot \frac{E_i}{E_0} \qquad \text{for } E_i \leq 1kV \qquad (11)$$

Where m_i … mass of ions, m_t … mass of atoms of the target, E_i … energy of ions, E_0 … sublimation enthalpy of atoms of the target, $\alpha = m_t/m_i$.

Sputtering yields for different gases and different materials of the target are usually examined by empirical way. For the most metals is the value of Y near to 1. For oxides and nitrides these values are usually from 0.1 to 0.2. The spectral yield does not depend on the temperature of the target and on the fact is the target is bombarded by ions or by atoms. Ions of the working gas can be, before they will fall onto the surface of the target, neutralized by free electrons, which are distributed in plasma. The spectral yield is strongly influenced by the direction of bombardment of target by the ions, by the energy of ions, by the material of the target, and by the mass of the ions.

Equations (8) and (9) can be completed by the equation, which describes dependence of the sputtering rate on next parameters of the process

$$x = \frac{M}{eN_A \rho} \cdot Y(E_i) \cdot j_i \qquad (12)$$

Where M … molar mass of the target, σ … density pf the material of the target, j_i … current density of the target, $Y(E_i)$ … sputtering yield, $e.N_A$ … 9.649 . 10^7 As/kmol.

During the intensive bombardment of the target with the ions of the working gas the temperature of the target increases. Its radiation can cause damage of the sputtered film, especially if the film is of an organic material. Properties of the film can also be influenced by the temperature of the substrate, which influences crystallinity and density of the growing film.

1.2 Factorial experiments

It has been shown that the theory of sputtering is very difficult and contains many parameters, which can not be found without special measurements. Therefore a method of factorial experiments has been chosen for construction of a mathematical model of the sputtering process [10]. The experiments of the type 2^3 have been applied. Following technological factors have been used for construction of the model: A … power of the plasma (W), B … pressure of the Ar (Pa) and C … flow of the oxygen or nitrogen (ml/min). The structure of the table of experiments is shown in Tab. 3.

TABLE 1. Table of factorial experiments of the type 2^3

A_1, A_2	… limits of the power of the plasma
B_1, B_2	… limits of the pressure of Ar
C_1, C_2	… limits of the flow of oxygen or nitrogen
$y_{m,n}$	… values of measured output parameter in the column *m* and the line *n*
R_i	… sum of values values of measured output parameter in the column *m*

First estimations of influence of combination of levels of the factors on the output parameters are calculated. Estimation of influence of the factor A is given by the formula

$$Z_A = a + ac + ab + abc - [(1) + c + b + bc] \qquad (13)$$

A_1				**A_2**			
B_1		**B_2**		**B_1**		**B_2**	
C_1	**C_2**	**C_1**	**C_2**	**C_1**	**C_2**	**C_1**	**C_2**
(1)	c	b	bc	a	ac	ab	abc
$y_{1,1}$	$y_{2,1}$	$y_{3,1}$	.	.	.	.	$y_{8,1}$
$y_{1,2}$	$y_{2,2}$	$y_{3,2}$	.	.	.	.	$y_{8,2}$
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
$y_{1,r}$	$y_{2,r}$	$y_{3,r}$	.	.	.	.	.
R_1	**R_2**	**R_3**	**R_4**	**R_5**	**R_6**	**R_7**	**R_8**

The characters *a*, *b*, c and their combinations are substituted in final calculations by the sums R_i at congruent columns. As shown in the equation (13), the estimation of influence of the level of the factor A on the output parameter Y is calculated as a difference between the results in the part of the Tab. 1 for level A_2 and the level A_1. By the same way the estimations of the influences of factors B and C are calculated. The calculated values of Z are used for calculation of testing characteristics that are compared with the critical value of the F-distribution for elected level of significance. The factors or their combinations, whose influence on the output parameter is low, are deleted of a mathematical model.

Before the model is constructed, the parameters are transformed. Transformation of the type

$$X_1 = \frac{2}{A_2 - A_1} \cdot \left(A - \frac{A_1 + A_2}{2} \right) \qquad (14)$$

is used for transformation of the factor A, and the same transformation is used for transformation of factors B (into X_2) and C (into X_3). The tested type of the model is usually a linear type completed by nonlinear combination parts

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_{n-1,n} x_{n-1} x_n + \beta_{1,2,3} x_1 x_2 x_3 + \ldots \tag{15}$$

The quality of the model is also tested using a F-test.

2. Experimental

Using the investigated sputtering process a capacitors with Al_2O_3 and AlN dielectrics have been fabricated. Their dimensions are shown in Fig. 3

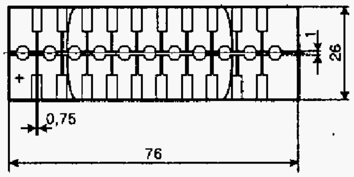

Fig. 3 Dimensions of sputtered capacitors. One capacitor has been fabricated by crossing of two perpendicular electrodes separated by the film of sputtered dielectrics.

The sputtering equipment has been of the type BALZERS PLS 160 (see) Fig. 4.

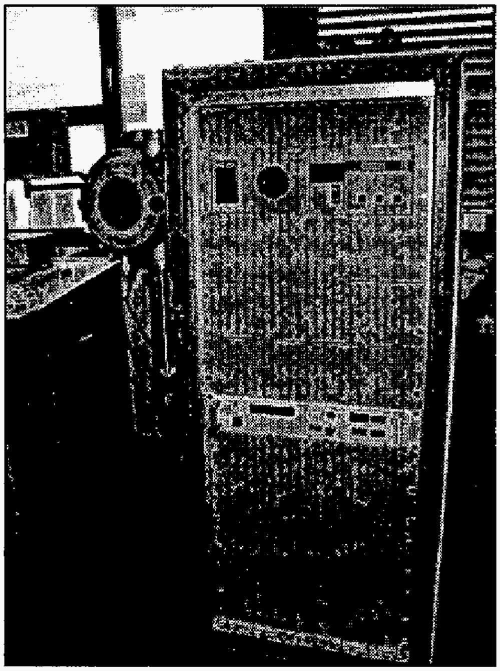

Fig. 4 Sputtering equipment BALZERS PLS 160

The capacitance and the loss factor have been measured using a semi.-automatic multimeter TESLA BM 595 RLCG. The measurement has been carried out at the frequency of 1 kHz and using the measuring voltage of 1 V.

Four mathematic models have been constructed:

- a model for calculation of the capacitance C_{Al2O3} of the capacitors with the dielectrics Al_2O_3

$$C_{Al2O3} = 5.935-0.0489a-1.722b-0.1c+0.00251ac+ \\ +2.112bc+0.0192ab-0.00128abc \tag{16}$$

- a model for calculation of the loss factor D_{Al2O3} of the capacitors with the dielectrics Al_2O_3

$$D_{Al2O3} = 0.00234-0.000084ab+0.0001a+0.0039b+ \\ +0.448.10^{-5}ac-0.000492c \tag{17}$$

- a model for calculation of capacitance of the capacitors with the dielectrics AlN

$$C_{AlN} = 0.970-0.0076a+0.206b-0.0021c+0.00015ac \tag{18}$$

- a model for calculation of the loss factor of the capacitors with the dielectrics AlN

$$D_{AlN} = -0.302+0.0023a+0.184b+0.0256c-.0012ab- \\ -0.0137bc-0.00017ac+0.000088abc \tag{19}$$

It has been confirmed by the additional experiments that the coincidence of the model with the results of the experiments is excellent. The differences have been less than 10 % for all investigated parameters.

An example of the dependence of the loss factor of the AlN films on the power of the plasma and the pressure of Ar is shown in Fig. 5. The figure has been obtained of the mathenatical model. Such the figures have been prepared for other investigated output parameters of the process and for other combinations of technological factors, too. Such the figures offer a very good outline about the mutual relationships of the investigated output parameters and the technological factors of the manufacturing process.

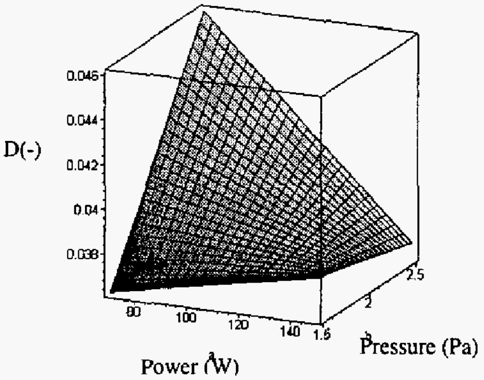

Fig. 5 The dependence of the loss factor of the AlN films on the power of the plasma and the pressure of Ar

Conclusions

Thin films of alumina and alumina nitride have been fabricated using magnetron sputtering process by the use of reactive sputtering. Quality of the films has been tested by the measurement of the capacitance and loss factor of fabricated capacitors with sputtered dielectrics.

The process has been analyzed by DOE. The factorial experiments of the type 2^3 have been carried out and mathematical models of the capacitance and the loss factor of the capacitors have been constructed. Quality of the models has been tested using the F-test. Coincidence of the models with the results of additional experiments has been examined. It has been found differences lower than 10 % between the results of the model and the experiments.

It has been found that the quality of the dielectric films fabricated by reactive sputtering is very good, and that the process is reliable with high repeatability. It has been also found that the method of factorial experiments can be successfully used for modelling of fabrication processes, whose analytical physical description is very complicated. The models give excellent results in whole range of limits of technological factors.

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