Study on the influence of the magnetron power supply on the properties of the Silicon Nitride films.

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Abstract. Silicon nitride (Si₃N₄) films were deposited by magnetron sputtering of silicon target in (Ar+N₂) atmosphere with refractive index 1.95 - 2.05. The results of Fourier transform infrared (FTIR) spectrophotometry showed Si-N bonds in the thin films with concentration 2.41·10²³ – 3.48·10²³ cm⁻³. Dependences of deposition rate, optical characteristics and surface morphology on rate of N₂ flow and properties of magnetron power supply.

1. Introduction

Silicon nitride (Si₃N₄) thin films are very promising due to its unique properties: high diffusion resistance to moisture and ions, high thermal stability, low level of surface state density, excellent insulating and semiconducting properties such as low level of leakage current, high breakdown voltage, satisfactory compatibility with semiconductive substrates in coefficient of thermal expansion. Due to its properties silicon nitride films are widely applied in microelectronics, e.g. as insulating layers in MIM-capacitors, masks for oxidation process and inhibitive coatings [1-6].

At present main technique to obtain silicon nitride thin films is plasma-enhanced chemical vapour deposition by decomposition of silane and ammonia (or nitrogen). But this technique has disadvantage – small fluctuation in operating parameters (pressure of gases, electrical power, gas ratio) leads to variation of another parameters. Such situation leads to difference in stoichiometric composition between Si₃N₄ and obtained thin films. Also, such thin films contain bounded hydrogen[1-6].

Magnetron sputtering is alternative technique allows obtaining stoichiometric silicon nitride thin films with good deposition rates and properties without toxic reagents (such as silane and ammonia) [1-6]. However in this case films’ properties depends on parameters of power supply: pulse rate, pulse duration etc.

This article is devoted to investigation of influence of the deposition parameters and characteristics of the power supply of the magnetron sputtering systems on the properties of the silicon nitride films.

2. Experimental

2.1. Magnetron sputtering

Silicon nitride thin films coatings were deposited on ion-plasma installation (figure 1). Vacuum system (3) based on a turbomolecular pump provided a residual pressure not less than 5·10⁻⁷ Pa. Pressure was measured by a wide-range vacuum gauge Micronol Plus (1).
Before deposition the substrates were cleaned using the ion source (2) with the parameters: voltage \( U = 2500 \text{ V} \), current \( I = 0.05 \text{ A} \). Ion cleaning time lasts 20 minutes. For film deposition magnetron was used (5) with planar silicon cathode and power supplies with different parameters:

- power source with two modes of operation: direct current (DC) and pulsed current with a frequency \( f = 100 \text{ kHz} \),
- current source with a frequency \( 134 \text{ kHz} \).

Deposition was carried out in the power discharge stabilization mode (0.5 kW) while maintaining a constant argon flow value (18 cm\(^3\)/min) and various values of the nitrogen flow (4.5 - 10.5 cm\(^3\)/min). Thin films were deposited on wafers made of monocrystalline silicon with intrinsic conduction.

2.2 Films characterization

The optical constants of films and their thicknesses were measured by ellipsometry, based on the analysis of changes in polarization state of a polarized monochromatic light reflected from the object at oblique incidence light beam (Ellips 1891 SAG device). Atoms’ bonds in coatings and their concentration were investigated by FT-IR spectroscopy method based on a study of the vibrational-rotational spectra (Infralum FT-801 instrument). The surface morphology was studied by scanning electron microscopy - method of solid surface analysis of microstructure with an electron microscope, which consists of viewing the reflected "electron image" (SEM Zeiss Supra 55 with electrons’ energy equal to 10 keV).

3. Results and discussion

During the reactive sputtering process, the greatest impact on the rate of growth of the thin film has a ratio between the plasma-forming (argon) gas and reactive (nitrogen) gas. Performance of the magnetron sputtering system according to the nitrogen flow rate \( Q (\text{N}_2) \) in the working chamber for different types of power supplies is shown in the figure 2.
Figure 2. The dependence of the deposition rate on the nitrogen flow.

Silicon nitride deposition rate decreases with the increasing flow rate of nitrogen into the chamber. This is due to the nitriding of the target, in which a thin layer of silicon nitride is formed on its surface, whose sputtering rate is significantly lower than that of pure silicon [7]. It should be noted that the power supply with the pulse rate 134 kHz has a high deposition rate at low flow of nitrogen. This feature is associated with formation of operating current pulses, providing a high pulse power at which silicon is sputtered more efficiently. However, due to the fact that the pulses are short enough, with increasing of nitrogen flow target is nitrided more rapidly and the rate of deposition decreases more intensively [8]. Using DC power supply allows getting close to the deposition rate with respect to the pulsed mode at a frequency of 100 kHz. However, using a magnetron DC causes the frequent occurrence of microarcs on the target’s surface that despite the operation arc protection system may have further effect on the quality of the coatings.

The dependences of the refractive index of thin films Si$_3$N$_4$ on nitrogen flow for different power sources are shown in figure 3.

Figure 3. The refractive index of silicon nitride films

The figure 3 shows that with increasing nitrogen flow the refractive index of coating decreases, regardless the type of power source. When using a current source with a frequency
of 134 kHz a more intensive decrease of refractive index is associated with the reasons described above for deposition rates.

Silicon nitride films have higher refractive index at low flow of nitrogen, which is associated with an excess of silicon. When nitrogen flow is 7-11 cm$^3$/min, films have refractive indices close to the stoichiometric Si$_3$N$_4$ ($n = 1.95 – 2.05$) [9].

By FTIR spectroscopy were investigated atoms’ bonds presented in the coatings and their concentration. The figure 4 shows a typical spectrum for all coatings on the example of the sample obtained at a nitrogen flow of 7.5 cm$^3$/min and using a power supply with the magnetron pulse frequency 134 kHz. The peak with the wave number of 840 cm$^{-1}$ indicates the presence of Si-N bond [9]. Also absence of any extraneous bonds is evident.

![Figure 4. FT-IR spectrum of Si$_3$N$_4$ film](image)

The concentration of the bonds (the density of the vibrating oscillators) Si-N in the films was calculated by formula:

$$\mathcal{C} = \frac{S}{\varepsilon} \quad (1)$$

where $S$ is the integrated intensity of the absorption band (peak area), $\varepsilon$ is the extinction coefficient.

Table 1 shows the results of calculated concentrations of bonds depending on the reactive gas flow into the chamber to a variety of magnetron power sources.

| Q(N$_2$), sccm | Concentration of bonds, n·10$^{23}$, cm$^{-3}$ |
|---------------|-----------------------------------------------|
|               | 100 kHz | DC    | 134 kHz |
| 4.5           | 2.86    | 3.38  | 2.41    |
| 6             | 3.07    | 3.24  | 2.58    |
| 7.5           | 3.52    | 3.11  | 2.76    |
| 10.5          | 3.28    | 3.13  | 2.61    |

It was found that all obtained coatings have similar values of concentrations of Si-N bonds. These values are consistent with the data for the plasma-chemical methods of Si$_3$N$_4$ films’ obtaining, which is a major in microelectronics at present.
SEM images of the samples were prepared for analysis of surface morphology, some of which are shown in figure 5.

![SEM images](image_url)

**Figure 5.** SEM-images of a surface test samples: (a), (d) - 100 kHz mode; (b), (e) - DC mode; (c), (f) - 134 kHz mode.

It was determined that the power source of the magnetron affects surface morphology. Thus the use of the DC power leads to the formation of the droplet fraction on the surface of the film (fig. 5b), due to the occurrence of electrical arcs on the surface of the magnetron target [10]. This is a disadvantage since it may reduce the performance of coatings. Pulse magnetron mode of operation avoids the problem of droplets (fig. 5 a, c). All obtained samples have a uniform homogeneous structure, including sections without droplets obtained at DC mode. The average grain size in the films, deposited by direct and pulsed current (100 kHz) are 20 nm, and the coatings produced by the pulsed current (134 kHz) - 50 nm.

4. Conclusions
As a result of the work, it was found that the deposition rate of Si$_3$N$_4$ films depends linearly on the flow rate of nitrogen into the chamber: increasing of N$_2$ flow reduces the rate. Also power supply has a negligible effect except for modes with a small flow of nitrogen.

Increasing the N$_2$ flow rate decreases the refractive index from 2.7 to 1.9. When the nitrogen flow rate is 7.5 cm$^3$/min and 10.5 cm$^3$/min refractive index films corresponds to the stoichiometric Si$_3$N$_4$ (n = 1.95 - 2.05).

The results of FT-IR spectroscopy showed the presence of only Si-N bonds in the films. Their concentration is practically independent on the parameters of the electric power of the magnetron sputtering system and is equal to (2.41 - 3.48) $\cdot 10^{23}$ cm$^{-3}$.

Scanning electron microscopy showed that all samples have a uniform homogeneous structure. The deposition of silicon nitride films in pulsed mode eliminates the problem of droplet fraction is typical for DC. The average grain size varies in the range 20-50 nm.

This work was financially supported by the Ministry of Education and Science of the Russian Federation, agreement no. 14.577.21.0204 of October 27, 2015. Unique project identifier: RFMEFI57715X0204.

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