Formation of dielectric silicon compounds by reactive magnetron sputtering

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Abstract. The paper is devoted to the study of reactive magnetron sputtering of the silicon target in the ambient of inert argon gas with reactive gas, nitrogen or oxygen. The magnetron was powered by two mid-frequency generators of a rectangular pulse of opposite polarity. The negative polarity pulse provides the sputtering of the target. The positive polarity pulse provides removal of accumulated charge from the surface of the target. This method does not require any special devices of resistances matching and provides continuous sputtering of the target.

1. Introduction
Dielectric silicon compounds in thin films are widely used in electronic technology. One of their special applications is the formation of thin-film dielectric membrane structures, such as shown in figure 1. These structures are the heat-insulating constructive basis of the sensitive elements for semiconductor gas sensors [1-3]. Membrane films for these structures can be obtained by the method of chemical deposition from the gas phase or by various methods of the vacuum sputtering. Vacuum methods, unlike chemical deposition, do not require using of toxic and explosive gases (such as monosilane, ammonia, etc.). It makes them more interesting in the practical application regarding safety [4].

Figure 1. Sensitive element on dielectric membrane structure: 1 – silicon substrate; 2 – dielectric membrane; 3 – structural elements (resistive heater, resistive temperature sensor, contacts to sensitive layer); 4 – sensitive layer; 5 – cavity under the membrane; 6 – thermal silicon oxide layer.

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Reactive ion-plasma sputtering is the most widely used vacuum method for dielectric film formation. In comparison to other methods, it allows obtaining dielectric films with better uniformity of composition and thickness. But, at the same time, it has the lowest sputtering rate. Initially the diode sputterers were used. Then triode sputterers were developed to increase the sputtering rate. For such sputterers, the increase of the sputtering rate is due to the increase of the gas ionization degree in the reaction chamber. For this purpose, an additional source of electrons is introduced into the sputterer – a thermionic cathode. Moreover, the presence of additional ions stimulates sputtering at lower pressures. This ensures better purity of the formed films [5].

Further increase of the sputtering rate was provided by the systems with reactive magnetron sputtering. Herein the target is located in the area of the magnetic field action. Electrons emitted from the target surface began to move along spiral trajectories. Thus, the probability of collisions of electrons with gas atoms was increased. It allowed increasing the gas ionization degree in the reaction chamber. Moreover, it also contributed to the improvement of the purity of the formed films. At present, the reactive magnetron sputtering is the most popular method for formation of dielectric compounds in thin films [5].

2. Formation of dielectric compounds

Reactive magnetron sputtering of the silicon target in the ambient of argon with nitrogen or oxygen was conducted in the unit UVN-71P3. For this purpose, the unit was equipped with the three-channel gas injection system in the reaction chamber. The especially pure gases were used for the study. The gas flows into the reaction chamber were controlled by electronic regulators of the gas rate.

In the process of reactive magnetron sputtering, formation of dielectric compounds may take place on the substrate surface, on the target surface with subsequent sputtering and in the gaseous ambient. Formed dielectric compounds are deposited both on the substrate and the target. The dielectric film gradually covers the target surface. Subsequently, the positive ions partially remove this film and are partially deposited on it. Thus, the target surface accumulates the positive charge. As a result, the negative voltage on the target decreases, and the glow discharge is extinguished.

To maintain the glow discharge it is necessary to remove the positive charge periodically from the target surface. Usually, this is done by supplying the alternating voltage of the industrial frequency 13.56 MHz to the target. For effective use of the power of the high-frequency voltage source, it is necessary to match the resistance of the glow discharge with the output resistance of the power source. For this purpose, special matching devices are used, which significantly complicates application of high-frequency power sources for supplying the magnetrons.

At present, the mid-frequency sources of pulsed voltage with the frequency of 10-100 kHz are widely used for deposition of dielectric compounds. These power sources do not require any special devices for resistances matching. To provide the alternating power supply for the magnetron in this work two power sources with opposite signs of the voltage supply were used. During the negative polarity pulse the sputtering of the target material was conducted. During the positive polarity pulse the removal of accumulated positive charge from the target surface was performed. The duration of the negative polarity pulse was equal to 40 μs, while the duration of positive polarity pulse was equal to 6.5 μs, and the pulse frequency was 36 kHz.

The feature of the magnetron sputtering is that only about 5% of energy of bombarding ions is expended on the sputtering process. The remaining energy is spent on heating of the target. The heating of the target has a significant effect on the deposition rate of dielectric films. To reduce this effect, it is necessary to provide continuous cooling of the target during the sputtering process. For this purpose, the base of the target (cathode) was equipped with the flowing water cooling system. But, as it turned out, the presence of the cathode cooling system does not guarantee the required heat removal from the target. Also, it is necessary to provide the acceptable heat contact of the target with the cathode.

The base of the target is the part of the copper cylinder with the diameter of 150 mm and the length of 320 mm. The target represents the cut of the silicon ingot with the thickness of about 1.5 cm. The
reverse side surface of the target is wavy, as it is shown in figure 2 (a). It does not provide the acceptable heat contact of the target with the cathode. To improve the heat contact, grinding of the reverse side surface of the target was conducted, as it is shown in figure 2 (b). Herein, to increase the magnetic field induction, the target thickness was reduced to 1 cm. It allowed reducing the pressure in the reaction chamber at sputtering. This allowed increasing the purity of the formed film.

After grinding, the target was fastened by screws to the cathode. Then, the target temperature at sputtering was studied. The results have shown insignificant improvement of the heat contact between the target and the cathode. To further improve the heat contact, the target was soldered to the cathode using the tin-lead solder. To provide the required adhesion level of the solder to the silicon, a layer of nickel was deposited on the reverse side of the target. Thus, the target temperature at sputtering was significantly reduced, which led to the increase of the sputtering rate.

![Figure 2. Silicon target (reverse side): (a) wavy surface; (b) grinding of the target surface.](image)

3. **Study of properties of obtained dielectric compounds**

The deposition rate, element composition and physical properties of dielectric compounds were studied. Pre-oxidized monocrystalline silicon wafers of orientation (100) with the diameter of 76 mm and with the thickness of (380±20) µm were used as the substrates for deposition of dielectric compounds. Oxidation was conducted in the ambient of dry oxygen at the temperature of 1000 °C. The oxide layer thickness was about 0.15 µm. Initially, substrates were washed for 10 minutes in the peroxide-ammonia solution at the temperature of 70 °C. Then substrates were washed in flowing deionized water of grade A. Immediately before deposition of dielectric compounds, in single vacuum cycle, the ion cleaning of substrates in the ambient of argon was conducted. The ion cleaning mode was as follows: the accelerating voltage - 1500 V, the ion current - 120 mA, the pressure in the reaction chamber - 0.83 Pa, duration - 3 minutes.

Deposition of dielectric films was conducted in the ambient of argon with oxygen and in the ambient of argon with nitrogen. It was revealed that the deposition rate of dielectric films depends on the power, supplied to the magnetron, as it is shown in figure 3.

The element composition of the obtained films was studied in the unit XSAM-800 of the company Kratos. The method of XPS (X-ray photoelectron spectroscopy) was used. The element composition was studied on the surface of the obtained films and in some depth after ion etching in the ambient of argon for 1 and 4 minutes. On the surface of the films a lot of contaminants were present, which were...
formed during storage between the technological stages. Therefore, the results of the element composition study on the surface of the films were not taken into account.

Figure 3. The deposition rate of dielectric films versus discharge power.

Figure 4 presents the composition of the dielectric films, which were formed in the ambient of argon with nitrogen. The column with the stoichiometric composition Si$_3$N$_4$ (right) is also shown for comparison. As can be seen in figure 4, these films contain the significant amount of oxygen and some amount of carbon. The presence of carbon in the films was caused by the oil of the forepump, which provides the preliminary pumping of the vacuum chamber. The presence of oxygen in the films was caused by its significantly higher chemical activity, compared to nitrogen. Oxygen gets into the vacuum chamber due to leakages from the external environment. Also, oxygen desorbs from the chamber walls and the equipment elements. Oxygen is reacting much faster with silicon than nitrogen, which is specially supplied into the reaction chamber. Thus, at the reactive magnetron sputtering, the oxygen absorption rate of the growing film significantly exceeds the nitrogen absorption rate. Moreover, the ratio of these rates strongly depends on the magnetron current. The increase of the magnetron current from 1 A to 5 A reduces the ratio of the oxygen absorption rate to the nitrogen absorption rate from 70 to 10. Consequently, to obtain the silicon nitride films with the minimum oxygen content, it is necessary to provide the sputtering of the target at the high power discharge. Also, the sputterer requires thorough hermitization of the vacuum system.
Figure 4. Element composition of obtained silicon nitride films: after ion etching during 1 minute (left), after ion etching during 4 minutes (right), for all samples.

The element composition study of the obtained films has shown that the oxygen content in the silicon oxide films and nitrogen content in the silicon nitride films depend on the magnetron current. With the increase of the magnetron current, the composition of the films approaches the stoichiometric one. For the silicon dioxide films, it corresponds to the ratio O/Si=2. For the silicon nitride films, it corresponds to the ratio N/Si=4/3. The silicon dioxide films, close to the stoichiometric composition, are formed when the magnetron current is about 1.2 A. The silicon nitride films, close to the stoichiometric composition, are formed when the magnetron current is about 4.5 A.

The influence of the magnetron supply voltage on the oxygen content in the silicon dioxide films was revealed. The increase of the supply voltage leads to decrease of the oxygen content in the film, as it is shown in figure 5. Herein, deviation from the stoichiometric composition of the film increases. In addition, some electrical parameters of the obtained dielectric films were measured. The measurements were made by the digital measuring device of type L, C, R. For this purpose, by using of magnetron sputtering through the mask, aluminum contacts with the size of 1×1 mm² were deposited on the surface of obtained films. The silicon substrates on the reverse side were completely covered with aluminum. Thus, the continuous contacts to the reverse side of the substrates were made. By the conductivity measurements of thus obtained MOS-structures, the resistance and the electrical strength of the films were estimated. The resistivity of the films is in the range of 5.2×10⁸ – 4.3×10⁹ Ω×cm. The dielectric breakdown voltage of the films is in the range of (3.1 – 7.4) ×10⁶ V/cm. This indicates good dielectric properties of the obtained films.
**Figure 5.** The ratio of the oxygen content to the silicon content in the silicon dioxide film versus magnetron supply voltage.

### 4. Conclusions

The formation processes of the dielectric silicon compounds by reactive magnetron sputtering of the silicon target in the ambient of argon with nitrogen or oxygen have been studied. At that, the magnetron was powered by the alternating pulse voltage with the frequency of 36 kHz. To improve the heat contact between the target and the cathode, the target was soldered to the cathode using the tin-lead solder. Thus, the target temperature at sputtering was reduced significantly, which led to increase of the sputtering rate.

It was revealed that the deposition rate of the dielectric films depends on the glow discharge power. It was shown, that the element composition of the obtained films primarily depends on the current and the voltage of the magnetron. To the lesser degree, it depends on the flow change of reactive gas into the vacuum chamber. To approach of the element composition of the films to the stoichiometric one, it is necessary to increase the current and reduce the voltage of the magnetron. When the current of about 1.2 A was supplied to the magnetron, the silicon dioxide films were formed, close to the stoichiometric composition. The silicon nitride films, close to the stoichiometric composition, were formed when the current of about 4.5 A was supplied to the magnetron. It was also revealed that during the formation processes of the silicon nitride films by reactive magnetron sputtering it is almost impossible to exclude the presence of oxygen completely in the film. This is due to the significantly higher chemical activity of oxygen, in comparison with nitrogen.

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