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MICRO-OXIDATION OF SILICON SURFACES BY MEANS OF ELECTRICAL DISCHARGES IN IMPULSE

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Articolul prezintă rezultatele strudiul teoretico-experimental privind formarea peliculelor de oxizi pe suprafeţele din siliciu cu ajutorul oxidării termice rapide în plasma cauzată de descărcările electrice în impuls. Procesul de oxidare a fost obţinut în atmosferă în condiţii normale. Se arată că proprietăţile peliculelor de oxizi depind de puterea disipată pe suprafaţa prelucrată, precum şi de materialul de bază a electrozilor.

Cuvinte-cheie: descărcare, oxidarea suprafeţelor din siliciu, pelicule de oxizi.

The paper presents the results of the theoretical and experimental study of the formation of oxide films on silicon surfaces by means of rapid thermal oxidation in plasma caused by electrical discharges in impulse. The oxidation process has been carried out under normal atmospheric conditions. It has been shown that the properties of the oxide films depend on the processing power as well as the electrode base materials.

Keywords: discharge, oxidation of silicon surface, oxide films.

INTRODUCTION

Oxidation is a chemical reaction between metal or semiconductor and an oxidizing agent (oxygen, ozone, water, carbon dioxide, etc.). The purpose of the oxydation of the samples surfaces of conducting [6] and semiconducting materials is the formation of protecting pellicles resistant to corrosion having high electrical resistivity, various radiation absorbability properties, etc. In a particular case of the oxidation of silicon samples the observed result was the formation of SiO_2 layer having dielectric and shielding properties determined by the process of adding controlled impurities. The SiO_2 structure is used as an insulating layer to separate different parts of the integrated circuit. By preserving semiconducting properties of the processed part, the technology of oxide films production on the semiconducting materials is very important since by preserving semiconducting properties of the processed part, it enables the wide use of these materials as the building elements in the electronics and microelectronics engineering industry. The formation of thin layers of SiO_2 on the silicon samples is fundamental for the concepts of constructional design and the technology of silicon devices for integrated circuits and nanoelectronic equipment [1].

Silicon oxidizes under the ambient temperature, in the atmosphere with oxygen content. But after the oxide layer reaches the depth of the 2-3 atomic layers, the layer grow stops. This phenomenon is explained by the the oxide layer protecting the silicone against its own further oxidation. In order to obtain the necessary depth of oxidized layers, the oxidation phenomenon is further activated by the temperature increase [4-5].

Folowing the classification [1], the methods of the silicon oxide layers formation can be divided into 2 basic groups. The first group includes methods based on the formation of oxidized pellicles by means of deposition from the outside. In other words the silicon piece plays the role of a nonreactive substrate. The second group contains the methods of direct oxidation of the silicon sample surface, when the oxide films are formed from the material of the subtrate by means of chemical interaction. Thermal oxidation of silicon is a very common technological approach, it is widely practiced in industry.

For the formation of oxide pellicles the following approaches are used:

- thermal oxidation in the presence of oxygen, called *dry oxidation* [1];

- thermal oxidation in the presence of oxygen and water vapour, called *wet oxidation* [1];
- thermal oxidation in the presence of only water vapour, called *steam oxidation* [1];
- oxidation by electrochemical means, called *anodic oxydation* [1];
- oxidation with the help of oxygen plasma, called the *oxidation in plasma* [4,5].

Often combined approaches are used.

The classical method of the silicon oxidation is thermal oxidation, performed by means of placing the processed material into a special furnace, so that to provide the diffusion and thermal oxidation in the oxidic medium. Under these conditions the oxygen contained in the oxidic medium reacts with the surface of the processed sample, heated and maintained in a certain thermal mode for a certain period of time in the furnace. Dry or wet (with water vapour) oxygen is used as an oxidic medium. The process of the sillicon oxidation is usually realized within the temperatures of 800-1300°C. This method requires a considerable energy and time consumption.

The oxidation in plasma may find a larger applicability due to the fact that the process of silicon oxidation occurs in a more intensive way in comparison to the „classical” oxidation.

The plasma for this approach can be obtained by two means:

- by the RF-discharge (microwave discharge);
- by the electric glow-discharge with a direct current.

The main purpose of the superficial oxidation of the sample by applying electric discharges in impulse (EDI) is the change in the properties of the surface layer of the sample, which is exposed to thermal or chemithermal processing in the plasma channel inside the interelectrode gap. In other words it provokes the activation of the processed surface (by means of heating, bombardment of ions, light emission, high-intensity electrical fields, etc.) And owing to the ionization of the components from the processing oxidizing medium and their acceleration in the electric field of the electric discharge there occurs its intrusion into the processed surface causing the change of material structure and thus of the layers properties [3].

THEORETICAL PREMISES AND METHODOLOGY OF EXPERIMENTAL INVESTIGATIONS

It is important to underline that the experimental investigations were performed in the normal pressure conditions at the indoor temperature. For the realization of the experimental investigations concerning the processing of semiconductor surfaces by applying the EDI plasma a special equipment was used: the electrical block-scheme of which is shown in Fig.1.

The equipment consisted of the following main parts: the block of power pulses which is a generator of RC-type pulses (G), the block of inducing (BI) and the block of command (BC). The command unit allows fine adjustment of the pulse repetion frequency within 1-300 Hz. The principle of the generator operation is based on the accumulation of a certain amount of the electrical energy in the capacitor battery and its discharging into the interelectrode gap in a short-time impulse (τ = 220 ms).

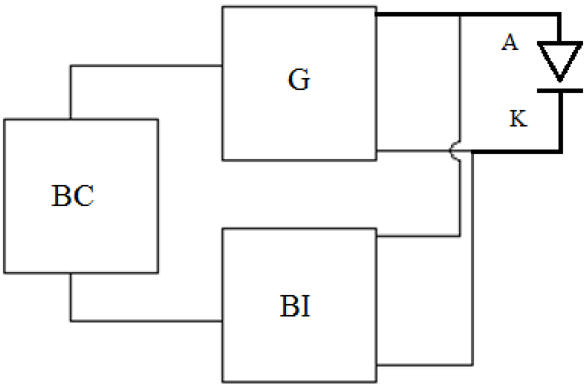

Fig. 1. The main electrical block-scheme of the equipment:
BC – block of command; G – RC-type pulse generator; BI – block of inducing

At the moment of piercing the interstice the electrons drawn from the cathode surface turn towards the anode. The electrons are accelerated in the interstice electric field, they collide with gas molecules and atoms in the interstice and produce the ionization of the working medium [2]:

$$O_2 \rightarrow O^+ + O^+ + 2e^-;$$
$$O_2 + O^+ \rightarrow O_3^+, \text{ etc.} \qquad (1)$$

The dissociation and recombination of the interstice medium take simultaneously:

$$O_2 + 2e^- \rightarrow O^- + O^-;$$
$$O_2 + O^- \rightarrow O_3^-; \qquad (2)$$
$$O^+ + O^- \rightarrow O_2;$$
$$O^+ + e^- \rightarrow O, \text{ etc.}$$

Thus the plasma channel formed in the interelectrode gap contains positive oxygen ions, which move to the processed sample surface under the action of electrodynamic force. Owing to this fact the activation of the semiconductor surface occurs, that causes its oxidation and difusion of the environment elements in the depth of the sample.

There are following reactions taking place on the silicon sample surface [5]:

$$Si + O_2 \rightarrow SiO_2 \qquad (3)$$
$$Si + 2H_2O \rightarrow SiO_2 + 2H_2.$$

In order to achieve the proper energetic balance necessary for the formation of the oxidized layer caused by interaction of plasma channel with the sample surface it is to follow certain conditions: the energy density of the processed surface must be less than specific heat fusion of the sample material [3]:

$$Q = \frac{4W_S}{\pi d_c^2 S} < Q_{top}, \qquad (4)$$

Q – is the energy released in the interelectrode gap, Q_{top} – specific heat fusion of the processed material $Q_{top} = q\rho$. The energy released in the interstice is one accumulated in the capacitor bank of the generator, taking into account η – its degree of efficiency in the interstice.

$$W = \frac{CU^2}{2}\eta. \qquad (5)$$

A range of experimental investigations were carried out using various dimensions of the interstice and charging voltage of the generator of RC-type impulses, that is varying the energy of the electric discharges in impulse, Fig. 2.

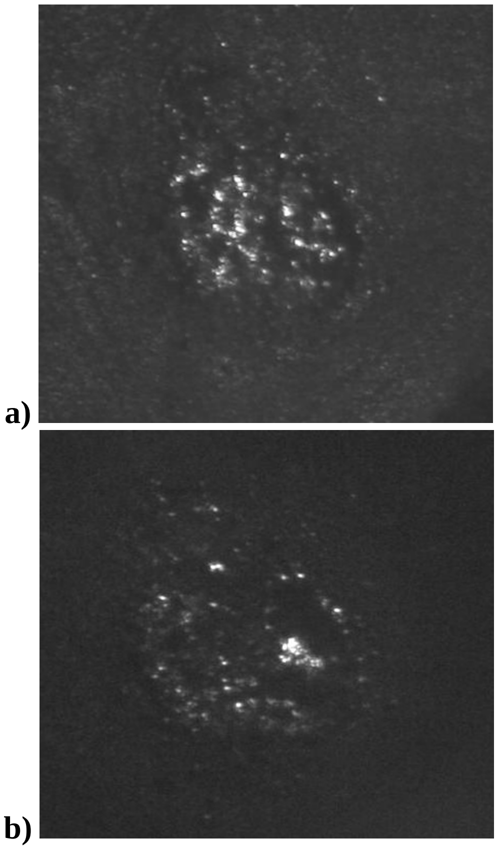

Fig. 2. Sample surface (sample-cathode) after processing EDI with tungsten electrode:
C = 8 µF, f = 16 Hz:
a) S = 1 mm, U = 100 V; b) S = 1,2 mm, U = 100 V

There are to observe erosion craters after the EDI processing of the sample connected in a traditional way into the circuit of the RC-type pulse generator, in the capacity of cathode. This fact attests that the appliance of the inductive impulses leads to the electrical breakdown of the semiconductor and results in the loss of the semiconductor properties. This effect occurs due to the excessive heating of the processed surface accompanied by melting, partial vaporization and uncontrolled solidification (in amorphous state) of the processed semiconductor.

For this reason there was designed and developed a technological scheme, which provides the formation of the oxide films on the semiconductor surface by means of EDI with indirect application (as presented on the Fig. 3).

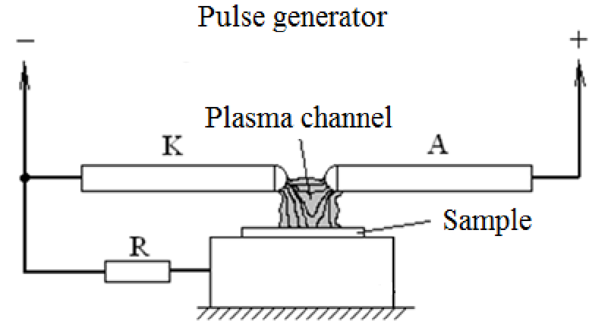

Fig. 3. Technological scheme of processing the semiconductor sample surface with indirect application of the plasma channel

For a precise control of the energetic mode the basic electrodes were sharpened cone-wise having 90° tip angle. Due to the fact that the processed semiconductor is connected into the discharge circuit by means of active resistance (R) of the MΩ order, the plasma channel resulting from the electric discharge between the basic electrodes, partially contacts with the sample surface changing its properties allowing to avoid its breakdown.

In the process of the experimental investigations the interstice size between the basic electrodes constitues $S_{e.b}$. = 2mm, and the distance between basic electrodes and sample: $S_{e.s}$. = 1,5mm. The material of the processed sample – Si (100).

THE RESULTS OF EXPERIMENTAL INVESTIGATIONS AND THEIR ANALYSIS

The processing of the semiconductor by means of EDI plasma according to the scheme presented on the Fig. 3 results in the formation of thin layer of oxide on its surface. The annealing colours appearing on the processed sample surface after the indirect application of EDI plasma prove that the oxide films were really formed (a dark brown layer).

The morphology of the semiconductor sample surface oxidized in the result of the EDI plasma application is presented on the Fig. 4 and 5.

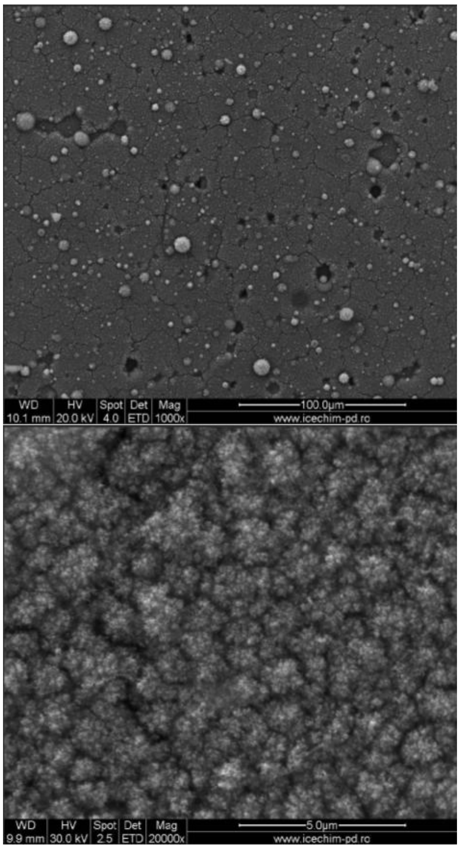

Fig. 4. The morphology of the semiconductor sample surface after the superficial oxidation applying plasma: the material of the basic electrodes – steel with low content of carbon; U = 100V; C = 100µF

The SEM analysis of the obtained films affirms that it essentially depends not only on the energetic conditions of processing, but also on the material of the basic electrodes. Thus we can state that usinng the steel electrodes results in the more pronounced and non-uniform structure of the oxide layer. The use of tungsten basic electrodes allows to obtain thiner and more uniform structure of the oxide films.

CONCLUSIONS

- the oxidation of surfaces by application of electrical discharges in impulse can be performed under the normal pressure conditions at the indoor temperature;
- the processed sample must be connected to the discharge circuit in the capacity of cathode by means of a resistance of the MΩ order;
- the morphology of the obtained pellicles depend on the energetic conditions of processing and on the material of the basic electrodes.

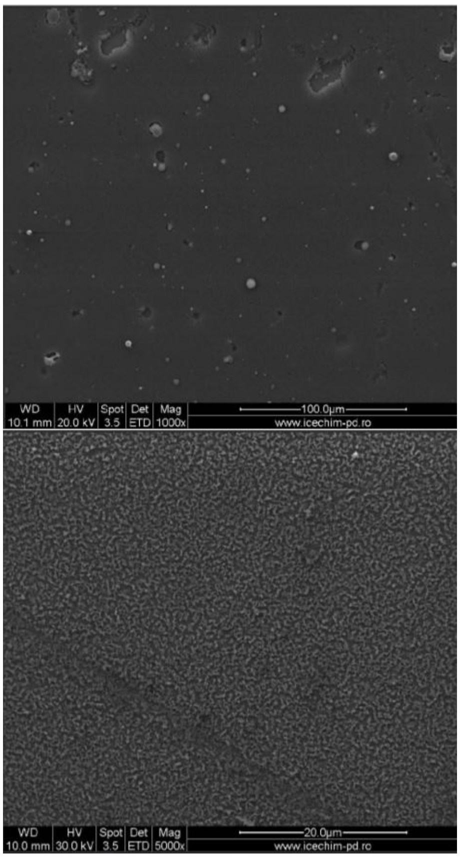

Fig. 5. The morphology of the semiconductor sample surface after the superficial oxidizing by application of plasma: the material of basic electrodes – W; U = 120V; C = 100µF.

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