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ELECTROLUMINESCENCE OF SILICON- AND SOME METAL OXIDES

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ABSTRACT

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Electroluminescence of silicon- and some metal oxides

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In the present work electroluminescence in Si-SiO₂ structures has been investigated. Electroluminescence has been recorded in the range of 250-900 nm in a system of electrolyte-insulator-semiconductor at the room temperature. The heating process of electrons in SiO₂ was studied and possibility of separation it into two phases has been shown. The nature of luminescence centers and the model of its formation were proposed. This paper also includes consideration of oxide layer formation. Charge transfer mechanisms have been attended as well. The nature of electroluminescence is understood in detail. As a matter of fact, electron traps in silicon are the centers of luminescence. Electroluminescence occurs when electrons move from one trap to another. Thus the radiation of light quantum occurs. These traps appear as a result of the oxide growth. At the same time the bonds deformation of silicon atoms with SiOH groups is not excludes. As a result, dangling bonds are appeared, which are the trapping centers or the centers of luminescence.

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SYMBOLS

Roman letters

A	anodic constant
d_{ox}	oxide thickness
E	electric field
E^*	critical value of electric field
f	function of excitation of luminescence centers
L	electroluminescence intensity
N	number of luminescence centers
n	concentration of luminescence centers
T	temperature
V_0	voltage drop
x_0	thickness of oxide layer

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INTRODUCTION

Si-SiO₂ structures are the basic part of microelectronics. To achieve the high perfection of insulator-semiconductor interface one needs to understand the processes occurring in the structures of this type. Therefore the properties of Si-SiO₂, which is produced using thermal oxidation of silicon, are of scientific and practical interest at present.

The systems of electrolyte-insulator-semiconductor (EIS) have benefits when one investigates electronic processes in Si-SiO₂ structures in presence of strong electric fields. EIS system allows to create stronger electric fields in oxide layer (up to 20 MV/cm) in comparison with metal-dielectric-semiconductor (MDS) structures. Also EIS system makes possible to control properties of insulator-semiconductor structures, using traditional microelectronics methods (current-voltage characteristic and capacity-voltage characteristic methods) and untraditional methods of proximate analysis such as electroluminescence of Si-SiO₂ structures.

In addition, creation of Si-SiO₂ structures is possible in EIS systems using anodic oxidation of silicon. This process exists when oxide layer is created with strong electric field which is attended inside insulator.

The main aim of the present work is to obtain the electroluminescent spectra of silicon- and metal oxides, such as tantalum- and niobium oxides. Using these results we try to explain electronic processes in Si-SiO₂ structures and anodic oxidation mechanisms in silicon in EIS systems and in metals in electrolyte-insulator-metal systems. After that, it will be possible to understand the role of electron subsystem and strong electric field in these processes. In other words, the goal of this study is to clear-up the oxide formation on silicon substrate using electroluminescence technique.

1. THEORETICAL PART

1.1 Properties and growing processes of oxides

1.1.1 Basic characteristics of Silicon

Silicon is a chemical element which has a label Si, atomic number 14 and atomic weight 28.0855 in periodic table of the elements. The oxidation states are -4, -3, -2, -1, +1, +2, +3, +4 (valence is IV). Silicon is in the third period of the periodic table of the elements. The electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$. Silicon is widespread on the Earth and in the Universe in general, but very rarely occurs as the pure free element. It is more widely distributed in form of silicon dioxide [1]. On the Earth, silicon is the second most usual element in the crust, making up 25.7% of the crust by mass. Silicon has many known isotopes, with mass numbers ranging from 22 to 44. ^{28}Si (the most usual isotope, at 92.23%), ^{29}Si (4.67%), and ^{30}Si (3.1%) are stable; ^{32}Si is a radioactive isotope produced by cosmic ray decay of argon [2].

Physical and chemical properties

Amorphous silicon is brown powder and crystalline silicon is a bluish-tinged, slightly glossy semiconductor (metalloid). Crystalline silicon forms face-centered diamond cubic crystal structure. This silicon oxide has a high durability and hardness. Silicon forms also face-centered cubic structure with a lattice spacing of 0.5430710 nm. Melting temperature is 1688 K, the boiling temperature is 3538 K, and the density is 2.3290 g/cm³.

Table 1.1. Physical and chemical properties

Name	Formula	Density, g/cm ³	Melting point, °C	Boiling point, °C
Silicon	Si	2.3290	1414	3265
Silicon dioxide	SiO ₂	2.2	1659 (±75)	2230

1.1.2 Basic characteristics of Niobium

Niobium is a chemical element with a symbol Nb, atomic number 41 and atomic weight 92.90638. The configuration of external electrons is $4s^2p^6d^45s^1$. Niobium is situated in the fifth group and in the fifth period of the periodic table.

Niobium is able to form oxides with the oxidation states +5 (Nb_2O_5), +4 (NbO_2) and +3 (Nb_2O_3). The oxides with the oxidation state +2 (NbO) occur rather rare [2].

Physical and chemical properties

Niobium is a glitter, silvery metal with body-centered cubic crystal structure. Melting temperature is 2750 K, the boiling temperature is 5017 K, and the density is 8.57 g/cm^3 . Niobium is chemically rather stable element. It reacts with most nonmetals at high temperatures. β -form of Nb_2O_5 is stable in normal pressure.

Table 1.2. Physical and chemical properties

Name	Formula	Density, g/cm^3	Melting point, $^{\circ}\text{C}$	Boiling point, $^{\circ}\text{C}$
Niobium	Nb	8.57	2477	4744
Niobium dioxide	Nb_2O_5	4.47	1380	

1.1.3 Basic characteristics of Tantalum

Tantalum is a chemical element which has a symbol Ta, atomic number 73 and atomic weight 180.94788. The configuration of external electrons is $4f^{14} 5d^3 6s^2$. Tantalum is situated in the fifth group and in the sixth period of the periodic table [2].

Physical and chemical properties

Tantalum is a grey silver, heavy, and very hard metal. In spite of hardness this metal has plasticity as well as gold. Tantalum has very high melting point ($2996 \text{ }^{\circ}\text{C}$). This metal has low-activity in normal state. Natural tantalum consists of two isotopes. Tantalum is able to form oxides with the oxidation states +5 (Ta_2O_5) and +4 (TaO_2). The most stable oxidation

state is +5, tantalum pentoxide. Tantalum forms an oxide (Ta_2O_5) only when the temperature is above 280°C [3].

Table 1.3. Physical and chemical properties

Name	Formula	Density, g/cm^3	Melting point, $^\circ\text{C}$	Boiling point, $^\circ\text{C}$
Tantalum	Ta	16.654	3017	5458
Tantalum dioxide	Ta_2O_5	8.23	1872	

1.2 Formation of oxide layers on silicon structures in strong electric fields

This section provides a brief overview of the current literature about the process of anodic oxidation of silicon. Below is considered kinetic regularities in different oxidation modes. Mechanisms of oxide growth are also given and information about electrophysical characteristics of Si-SiO₂ structures, which are obtained by anode oxidation, is provided.

The processes of forming niobium oxide are described in details in Master's thesis of A. Fadeeva [4]. Oxidation processes for other barrier (valve) metals such as tantalum and titanium are almost the same like for niobium.

1.2.1 Anodic oxidation films and materials for its formation

The anodic oxidation of silicon (or electrochemical anodizing) is oxidation of silicon electrode in the electrolyte. The particle transport of silicon through the SiO₂ layer in the form of ions is realized by electric field in this process [5].

The main difference between the methods of anodic and thermal oxidation is that the oxidation is done in room temperature. In case of anodic oxidation the mechanical stresses at the border of the Si-SiO₂ structures are missing. The possibility to control the thickness of oxide layer and properties of the boundary of Si-SiO₂ structures is appeared during the film growth processes [6].

Properties of the anodic oxide films (AOF) depend strongly on the pretreatment of oxidizing surface, the electrolyte and the oxidation regime. This apparently explains some differences between the results of the AOF formation and electrophysical characteristics of AOF obtained by different authors [5, 7].

The first experiments of the silicon anode oxidation have shown that oxide films contain large number of pores. Different aqueous solutions of acids and salts were used as a forming electrolyte.

Electron microscope studies showed that the films contain a large number of pores. The size of these pores increases as a forming voltage and current increase, and can reach 50 nm in a crosswise. The AOF which were described above have been grown in the aqueous solution of boric acid. On the other hand the films, which have been obtained in the aqueous solution of KNO_3 in the N-metilatsetamid ($\text{CH}_3\text{CONHCH}_3$), don't have pores.

Further studies of Si-SiO₂ structures showed that the porosity of oxide layers and other electrophysical parameters of structures are the best when organic solvents are used as a forming electrolyte. Organic solvents, such as N-metilatsetamid and ethylene glycol, containing a small additions of inorganic acids (or salts) and water, are good for these purposes [8, 7, 9]. All information above is for Si-SiO₂ structures which are formed using anodic oxidation.

The most frequently used solution is 0.04 N solution of KNO_3 in the ethylene glycol with the addition of water. Mixing of electrolyte provides uniform growth of AOF [5].

1.2.2 Different modes in anodic oxidation technique

Anodic oxidation of silicon can be carried out in galvanostatic mode (constant current through the sample), in controlled potential mode (sample constant voltage) or in various combinations of these two regimes.

Oxidation kinetic is usually described by the dependence of the sample voltage drop in galvanostatic mode on time. There are a lot of investigations about anodic oxidation of silicon in this mode. The analysis of these investigations is allowed to assign some general

mechanisms marked by almost all authors [7, 8, 10]. Nonlinear dependence of the sample voltage drop on oxidation time is observed at the initial time of kinetic process. The existence of free charge carrier depletion in space-charge region in semiconductor explains this fact in studies [11]. The dependence of voltage on time becomes linear at a certain output voltage. It is possible to control the thickness of oxide film during its formation. The oxide film voltage drop can help to make the control [12],

$$d_{ox} = A \cdot V_0, \quad (1.1)$$

where d_{ox} is the thickness of oxide layer, V_0 is the voltage drop in oxide layer and A is anodic constant.

The value of A varies in the range of 0.4 nm/V up to 0.6 nm/V in case of oxidation in ethylene glycol and from 0.4 nm/V to 1.36 nm/V in methanol [13].

There are some difficulties to control the thickness of AOF during the oxidation of the silicon. This is explained by the necessity for precise definition of voltage drop in the silicon substrate and the electrolyte. Significant errors in thickness determination of the AOF could be in case of inaccurate assessment of V_0 . Growth kinetics of AOF on n-type silicon substrate are investigated in studies [12]. The samples have been exposed for a short period of time to determine voltage drop on the silicon substrate. Nevertheless, there is no sufficient reason to believe that this procedure completely eliminates the existence of space-charge region in silicon. Furthermore this exposure essentially could affect the nature of the oxidation process.

Because of the relationship between the thickness of AOF and the voltage in the oxide layer, the average electric field in the oxide layer is constant in the process of oxidation. In case of silicon oxidation it is about 20 MV/cm. The growth rate of oxide film rises with the current density of formation increasing.

There is a maximum voltage value when the voltage dependence of the time becomes sharply nonmonotonous. Oxide film begins to break down. Therefore the thickness of oxide layer formed in galvanostatic regime will be less than 150 - 200 nm.

The formation kinetic of AOF on silicon in potentiostatic regime can be described by the time dependence of current that flows through the structure. Current that flows through the structure is inversely proportional on time of AOF's formation in this regime. At the same

time oxide layer thickness increases with the time in logarithmic way. Therefore, the thickness of AOF is proportional to sum charge which flows through the structure.

Current flow through the structure is reduced because the average field strength decreases. On the other hand it could be explained as structural changes in oxide during the growth of its thickness [10].

A combination of two regimes described above gives structures with the best parameters for the built-in charge, for the density of surface states and leakage currents, and for the stoichiometry. As a rule, the following procedures are used for the oxidation. First, oxidation of silicon to a given thickness (voltage) is performed in galvanostatic mode. Then forming process is carried out in potentiostatic mode. It lasts until a certain value of forming current density will not be reached or simply during certain period of time. Thus, the decreasing of molding current leads to an improvement of quality of the structures. Therefore the rate of oxide growth in the final phase reduces. Apparently, the low rate of oxidation brings to the structural changes in the oxide layer. These changes are probably improved parameters of layer [14].

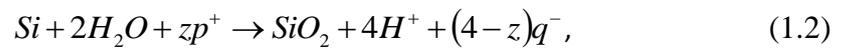
Combined mode described above matches best from galvanostatic regime and potentiostatic regime, namely: a high average rate of oxidation (90 % of the thickness of oxide layer increases in galvanostatic mode [11]) and low final speed of the process.

Reaction efficiency is the ratio between anodic current, which forms the oxide, and total current. Efficiency of anodic oxidation current in case of oxidation of silicon is 1 - 2% [7, 8]. The reaction efficiency is more than 2 % initially. As opposed to that the reactions of anodic oxidation of valve metals has efficiency which is close to 100 %. It should be noted that in [15] were observed efficiency which was close to 100 %. It was at the initial stage of silicon oxidation. The oxide layer thickness was less than 2.5 nm. Thus, when the thickness of oxide film is more than 2.5 nm the major part of current, associated with electrons transfer or holes, goes through the oxide layer.

1.3 Mechanisms in dioxide structures during the formation processes

1.3.1 Electronic mechanisms

Significant influence of electron-hole current through the sample on mechanisms of formation of Si-SiO₂ structures and its electrophysical characteristics is well known [14, 10]. However, the issue of electron-hole subsystem in the process of anodic oxidation of silicon is still open. Contradictory statements exist in the literature concerning the role of the holes. For example, in [16] it is noticed that holes take part in anodic oxidation process. It is shown in this reaction:



where $2 \leq z \leq 4$.

It can be assumed that holes take part in the anodic oxidation because some differences in the initial phase of the formation kinetics appear for n- and p-type [11]. At the same time there is strong dependence of the kinetics of formation on illumination in intrinsic absorption band of the silicon. Apparently, this band is connected with generation of nonequilibrium holes in the surficial region of silicon [11, 12, 14]. When high-intensity illumination is applied, formation kinetics for n-type silicon will overlap with the formation kinetics for p-type silicon. Increasing the concentration of holes in the surface area of a semiconductor can influence on the kinetics of formation of oxide layers in two ways. First, the behavior conditions for chemical reaction described above are improved. It occurs because of increase the concentration of holes. Secondly, concentration of holes in space-charge region is changed. It leads to redistribution of voltage drop between the substrate and the oxide layer. As a result, it can eventually change the formation mechanism of oxide layer.

However, the proceedings [11] show that the change in the concentration of holes in the substrate does not influence the linear parts of formation curves. In consideration of this information one could make a conclusion that anodic oxidation process is controlled by processes inside this oxide. Moreover, the decreasing of holes concentration as a quasiequilibrium conditions in space-charge region leads to increasing of growth rate of oxide almost by an order of magnitude. In article [12] is reported that at the initial stage of oxidation the oxidation rate of n-type silicon in darkness is bigger than the oxidation rate

of p-type and n-type silicon in light. Such dependence was observed also on the linear formation plots. It should be noted that the authors have not used direct method for measuring the thickness of oxide. They tried to find out the thickness of oxide layer using the measurements of voltage drop on the structure during the short-time illumination [12].

The differences in formation kinetic on linear range in [12] are absent because of possible redistribution of dope in silicon during the growth process. This behavior also occurs through the formation of extra silicon atoms. These atoms are redundant with respect to stoichiometric composition. Author finds that the disappearance of the differences associated with restoration of quasiequilibrium conditions in space-charge region in silicon. The restoration of quasiequilibrium conditions holds by increase of charge carrier ability to generate and recombine on the surface of substrate during the oxide growth. This assumption is confirmed by the results of the article. The surface recombination speed achieves its maximum in room temperature (10^6 cm/s) when oxide layer thickness has reached a few hundred angstrom. There is also second possibility of the disappearance of the differences. Hole current component decreases when thickness of oxide reaches a certain value. In other words, the order of participation of the holes in the anodic oxidation is reduced [14].

1.3.2 The nature of luminescence

It was found in papers [6, 14] that anodic oxidation of silicon is gone with illumination of the oxidizable sample in the wavelength range 380 - 600 nm [6]. In many of articles such luminescence was interpreted as chemiluminescent models. According to these models, the illumination is due to excitation of hydroxyl radicals in chemical interaction with ions of a semiconductor. Other researchers have suggested that this luminescence depends on the interaction of injected electrons in the oxide film with SiO₂ matrix [14]. In other words, this process has fluorescent nature. The authors of other article linked the existence of the luminescence with radiative recombination via surface states on the interface of Si-SiO₂ [17].

There are some facts such as the linear growth of luminescence intensity with increasing thickness of the AOF, the existence of luminescence of the samples in unoxidizable electrolytes, the spectra of luminescence for anodic oxidation are similar to spectra of the

cathode- and photoluminescence structure Si-SiO₂. Taking in consideration of these facts it is possible to conclude this fluorescence has electroluminescent nature [14].

1.3.3 The ion transfer mechanisms

In several papers ones tried to find out what is dominant in the process of anodic oxidation: the transfer of anions (oxygen ions), or the transfer of cations (silicon ions) through the oxide layer [14, 6, 10]. In contrast to the thermal oxidation of silicon the growth of the AOF happens on the outer boundary [17]. Silicon atoms are separated away from the substrate via a strong electric field. After that silicon atoms in form of ions are transported through the dielectric layer.

In papers [10] is suggested that the bond breakage of silicon occurs through electrons heating in conduction band of oxide. It goes with impact ionization. Strong electric fields ($E_{ox} > 10$ MV/cm) always accompany the process of anodic oxidation. At the same time, authors of paper [18], using the electrolyte with tritium, showed that negative hydroxyls ions may take part in the oxidation process. Hydroxyls injects in the oxide from the electrolyte. It appears even if the formation current is less than 3 mA/cm².

Nevertheless, all currently available data about electrophysical and physicochemical characteristics of Si-SiO₂, which were obtained by anodic oxidation, comes to the cationic mechanism of oxidation [14].

1.3.4 The influence of various impurities on the formation mechanisms

It is studied how presence of water in electrolyte influence the formation process, the structure and electrophysical characteristics of structures. The studies have shown that the oxygen, which forms the oxide, comes from the water (80 - 90%) and inorganic salts (10 - 20%), such as KNO₃ [14]. The investigation mentioned above have used radioactive isotopes. The paper [18] suggested that water molecules penetrate only the top layer of oxide and dissociate in it during the anodic oxidation. Consequent diffusion takes the form of hydroxyl groups, which are major sources of oxygen. This oxygen goes to oxide formation.

The materials which were received during the anodic oxidation of silicon have almost the same chemical structure as the materials obtained in thermal oxidation [11].

In both cases, bulk oxide has chemical composition which corresponds to the formula SiO_2 . Only in the surface area of anodic oxide an excess of silicon atoms was found ($\sim 6 \cdot 10^5 \text{ cm}^{-2}$). Mass spectroscopy of secondary ions showed that approximately one third of the thickness of oxide layer at its inner interface is characterized by low yield of Si^+ atoms and increased yield of $(\text{SiH})^+$. These oxides have been obtained using the anode oxidation in galvanostatic mode (thickness is up to 100 nm) without further annealing.

This fact can be explained by layer, with significant oxygen deficit, at the border of the silicon-oxide. The layer contains a large quantity of unsaturated silicon bonds. The same articles show that the polarization of thermally oxidized silicon in electrolytes leads to an excessive concentration of silicon oxides in the inner boundary structures.

Therefore it is possible to talk about cationic model of anodic oxidation [14]. The cation distribution on the thickness of oxide layer at the time of switching off the electric field is the reason for concentration gradient of excess silicon atoms. In other words the concentration of excessive silicon atoms gradually decrease when one moves away from the Si-SiO₂ interface.

In the paper [6] is shown that the etching rate of silicon anodic oxide films is higher than etching rate of thermal oxide films. This indicates either these structures have high friability, or a large number of impurities present. Etching rate of anodic oxide is significantly reduces when the structures are annealed at 300°C. In this case the etching rate is almost the same as for thermal oxide films.

The refractive index of anodic oxide films is similar to refractive index of thermal oxide films (1.46 - 1.48). This number decreases when the thickness of oxide film or water concentration in electrolyte increases.

The final electrophysical parameters and the properties of the interface will be different if one uses different mechanisms of oxidation [14]. There are high density of surface states, dependence of the magnitude and polarity of built-in charge in oxide layer on oxidation

conditions, high density of traps in the oxide layer and changing the value of charge under the influence of ultraviolet radiation [14]. All features mentioned above were ascertained during analysis the interface when the AOF was being formed.

As it was already mentioned above, the structure of Si-SiO₂ which was received using anodic oxidation of silicon, have rather high density of surface states ($\sim 10^{13} \text{ cm}^{-2}$). It is slightly reduces when the growth rate of oxide is small and finite. Annealing reduces the density of surface states to the values which are usual for the thermal oxides. The anneal temperature was 250 °C [13]. The authors of paper [14] tie the reduction of surface states density with continuation semiconductor-insulator interface's oxidation. Oxidation process goes in potentiostatic mode.

In article [12] is studied effect of holes concentration in a semiconductor on the quantity and sign of built-in charge. When the hole concentration of in the substrate is large (n-type silicon in the light or p-type silicon), the total charge in oxide is positive. When the concentration of holes is low (n-type silicon in the dark), the sum charge is negative. The reduction of current density of formation results in decreasing of reduced oxide's growth rate. It leads to increasing the total positive charge [14].

1.3.5 Two stage formation model

In the theory there are two stages in the formation of the electrophysical properties of structures which come out of silicon anode oxidation.

Firstly, there is a formation of surface and trap states in oxide. This type of formation connects with ion processes. Secondly, there is formation of built-in charge in oxide. This type of formation sets conditions for electronic processes in oxide [14].

Thus, the electrophysical characteristics of Si-SiO₂ structures, which were obtained during an anodic oxidation of silicon is significantly inferior to structures formed in the course of thermal oxidation. That kind of structures have higher degree of oxide disorder, thickness inhomogeneity of oxide, large length of transition layer at the interface of Si-SiO₂ and large disordering at this interface. As a result, there are higher built-in charge and density of surface states in the structures, which were obtained during anodic oxidation of silicon.

In conclusion, it should be noted that several issues related to the formation processes of the anodic oxide films on silicon remains open at present. First of all, the mechanism of oxide's growth has not been clarified. It is unclear whether there are one or more mechanisms. It is just conditional sorting of formation curves per the initial and finite areas. Systematic study of the thickness dependence of oxide layer on its formation time was has not carried out. Secondly, it is not clear how electron and hole components of current influence on processes of forming the oxides and formation the electrophysical characteristics of the structures Si-SiO₂. Second question is why the electrophysical characteristics of the AOF on silicon receive much worse than it is during the thermal oxidation. Possibly, degradation of oxide layer is running concurrently with the process of formation. It occurs when the large electronic current passes through the oxide.

Fluorescent techniques enable to solve the issues mentioned above more flexible. These methods are available to study both the mechanism of anodic oxidation and finite parameters of producing structures. Using this method one can simplify the interpretation of results described above and resolve existing problems and contradictions.

1.4 Insulator-semiconductor structures investigated by fluorescent techniques

Main application of fluorescent techniques is to study the properties of insulator-semiconductor structures. Present study considers basic abilities of electroluminescence (*EL*) in the electrolyte-insulator-semiconductor (*EIS*).

Fluorescent techniques are usually classified according to the method of luminescence excitation. The main methods of excitation are as follows: excitation by light (photoluminescence technique, *PL*), high-energy electrons excitation (cathode-luminescence, *KL*) and the excitation using electric field energy. In case of *EL* electric field is localized in the dielectric layer.

Photoluminescence (*PL*) is the most accepted technique in solid state physics and informative in terms to clarify the energy levels of the luminescence centers. This

technique enables to receive both the radiation spectra and the luminescence excitation spectra. Photoluminescence has been used intensively to study the amount of crystalline and vitreous SiO₂ [4, 19, 20]. In investigations a number of emission characteristic broad bands were found. These emission bands associated with the SiO₂ matrix. The series of bands depends on the presence of luminescent impurity centers in silicon dioxide. These bands are located in energy values 1.9; 2.2; 2.7 3.2 and 4.3 eV. Different sets of spectral bands with the same method of excitation are observed by different authors. The identity of photoluminescence spectra in crystalline and amorphous SiO₂ shows that defects which are responsible for appearance of these spectra are the same. It is possible to assume that luminescence appears as a result of imperfection existence. These defects are placed in SiO₂ and have a nature of point defects [20].

It is difficult to use *PL* to study thin films. Problems are connected with low efficiency of excitation and with small analyzable volume. A photoluminescence spectrum for Si-SiO₂-Si_{poly} structure has been obtained using the laser with wavelength 441.6 nm for excitation. The thickness of oxide layer in Si-SiO₂-Si_{poly} structure was 120 nm. This spectrum looks like a broad band with a peak near 2.4 eV. This maximum is connected with the processes of radiative recombination through the wide area of impurity in a band gap of SiO₂. The spectral distribution of photoluminescence in Si-SiN_x ($x < 4/3$) structures corresponds to a broadband radiation in the range of 1.8 - 3.2 eV. This fluorescence was connected with radiative recombination through the electronic states in a band gap of dielectric (Pul-Frenkel's centers) [21, 22].

Cathode-luminescence (*CL*) method allows to investigate the dielectric layers, which have thickness even several angstroms. Using this technique, one can obtain information about spatial localization of luminescence centers. It could be reached by recording a dependence of luminescence intensity in defined spectral region on the energy of excitation beam [23]. Formation of new defects in the dielectric layer is the main disadvantage of the cathode-luminescence technique. New imperfections appear under the influence of electron beam with energy of several keV.

There is a series of broad band of emission with energies 1.9; 2.2 - 2.3; 2.7-2.8 and 4.3 - 4.4 eV. These broad bands are observed in cathode-luminescent spectra of the Si-SiO₂ structures, which were obtained using anodic and thermal oxidation. Influence technique of forming oxide layer on the band's intensity in the spectra of the *CL* was determined [23].

Cathode-luminescence of the Si-SiN_x ($x \leq 4/3$) structures was studied in [24]. Luminescence was registered in the range from 1.5 eV to 5.5 eV. It looks like a continuous superposition of components and a set of characteristic radiation bands with energies 1.75; 2.0; 3.2 and 4.6 eV. Band of 3.2 eV is most clearly defined in the spectrum. The intensity of that band increases with the concentration of ultra stoichiometric silicon in a silicon nitride.

Using electroluminescence to study the properties of Si-SiO₂ structures was started in paper [25]. EL spectrum consisted of two radiation bands with energies 3.2 and 4.7 eV. Radiative electron trapping in a band gap of the SiO₂ explain the features of EL spectrum. In the sequel EL technique was developed and used to study insulator-semiconductor structures [26, 27].

It is assumed in papers [26, 27] that electroluminescence in Si-SiO₂-metal structures consists of two components. The first component is luminescence which is defined by radiative relaxation of plasmons. Hot electrons entering from the oxide layer excite plasmons in metal electrodes. Luminescence excited in a bulk oxide layer is the second component. In the last case, the authors noted the existence of three radiation bands in the electroluminescence spectrum (1.8, 2.8 and 4.3 eV). The intensity of peaks depended on the concentration of excess silicon in SiO₂. The band of EL (3.7 - 3.8 eV) appeared after enrichment of SiO₂ with excess silicon. All the observed electroluminescent bands were connected with transitions in the defects of one type - clusters of the silicon.

2. EXPERIMENTAL TECHNIQUE

2.1 Synthesis of silicon oxide

To obtain electroluminescent spectra a special sample holder was created (Fig. 2.1). It was made of Teflon and had a form of hollow truncated cone. Quartz glass closed the base of a cone. The test specimen is pressed to the hole in the top of the cone basement. As a result, the semiconductor-insulator-electrolyte system was obtained. Ohmic contact to the semiconductor substrate was made using indium-gallium eutectic.

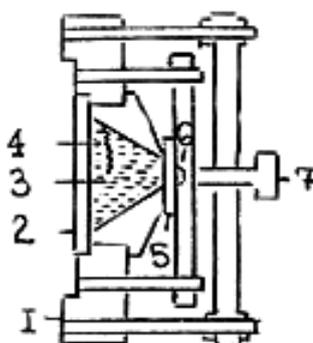


Fig. 2.1. Electrochemical cell to study *EL* in the EIS-system: 1 is body; 2 is quartz window; 3 is electrolyte; 4 is polarizing electrode; 5 is test sample; 6 is ohmic contact to semiconductor; 7 is clamping screw.

Wavelength-scanning was performed using monochromator MS257. Experimental results are automatically saved on the computer as a data file.

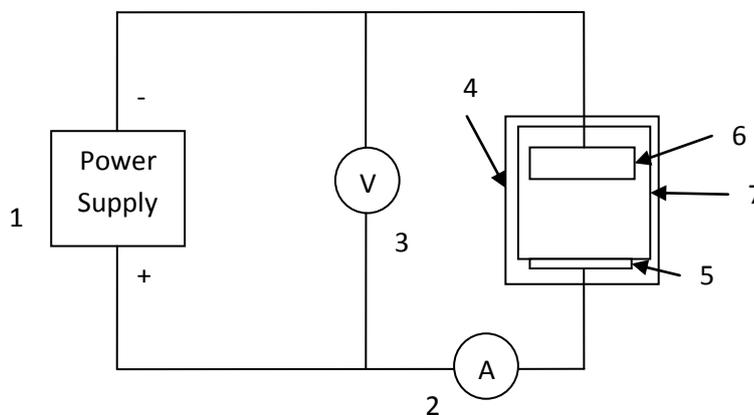


Fig. 2.2. Equipment scheme for oxide formation: 1 is power supply; 2 is ammeter; 3 is voltmeter; 4 is sample holder; 5 is a sample; 6 is polarizing electrode; 7 is electrolyte.

All measurements were made at the temperature of 293 K. Installation for anodic formation of insulator-semiconductor structures and studying processes of anodic oxidation (Fig. 2.2) consisted of a power unit and the electrochemical cell (sample holder). This system allowed to carry out the oxidation of the structures using galvanostatic mode, potentiostatic mode or combination mode.

The range of current density in galvanostatic mode was 0.5 - 30 mA/cm² when the square of oxidizing sample equals 1 - 2 cm². Formation voltage in potentiostatic mode is in the range of 1 - 299 V. The accuracy of current and voltage stabilization was not worse than 1 - 2%.

2.2 Description of installations for measuring EL spectra

The installation, described below, was used to measure the spectra of electroluminescent at *Lappeenranta University of Technology*.

Measuring system consist of several parts. The main part is monochromator and spectrograph (MS257) and radiometry system (Merlin) which are produced by Oriel Instruments. Other equipments are needed for measurements as an auxiliary part.

System is controlled by PC thought the instrumentality of special program TracQ.

Monochromator has quadruple grating with 1200 lines per millimetre and motor driven slit assembly on input and each outputs. These slits are continuously adjusted from 4 micrometre to 2.3 millimetre in width. Therefore this equipment particularly covers wide wavelength range. There are one input and two output ports. The standard configuration for MS257 is for the output beam to exit via the axial port. It is required to replace side exit mirror to adapt monochromator for use with another output port. Quadruple-grating turret drive, motor driven flip mirror, motor driven slit assembly and integrated shutter are controlled automatically via special program, which is needed to install on PC. Communicating with MS257 is provided via the IEEE-488 interface (GPIB interface). It is used GPIB-USB converter for sending commands to spectrometer from the PC.

Radiometry System (Merlin) consists of a chopper, a detector head and the Merlin control and processing unit. The chopper modulates the measured signal. The detector head senses the chopped radiation the zero level as the blade blocks the beam. The control unit drives the chopper and acts as a lock-in amplifier retrieve the signal and ignore detector signal

from un-chopped radiation. The Merlin has main screen and three menu screens provide access to the powerful signal processing and set up capabilities which are possible. The main screen gives possibility to look through the measurement information. The menu screens are used for changing the instruments set up such as the filters and chopper managing, the selection of synchronization source and other useful options. Merlin also provided communication with a PC via the IEEE-488 interface (GPIB interface). Possibility to manage some parameters and sets up of radiometry system is available for PC's users.

The TRACQ data acquisition software was designed to automate repetitious spectral measurements of an unknown light sources or samples. This software controls the individual components of the whole measuring system. Different arithmetic operations with spectrum and some scan modes are available using the TRACQ software.

Two different detector types, silicon photodiode detector and Photomultiplier tube (PMT) was available. The PMT was chosen because the wide wavelength range is needed and high responsivity in UV area of wavelength range. Side-on PMTs are more economical and has a responsivity peak at 400 nm. Besides it has wide wavelength range (160 - 900 nm).

Silicon detector has also wide wavelength range, but the detector responsivity in UV range is not so good. It is required good response in experiment because of the small signal intensity.

This optical system requires the use of a chopper to modulate the light beam either because detector does not respond to continuous radiation or because the signal to noise ratio can be improved by modulation and filtering techniques. In most cases it is better to place the chopper as close to the radiation source as possible. If the chopper is placed close to the detector, then all radiation entering the detector will be chopped and recognized as the signal. Background radiation will contribute to the measured result.

Measurements were carried out also in *Petrozavodsk State University*. The installation, which was used there, is not completely automatic, but has almost the same performance.

Measuring system consist of monochromator (MДP-41) and radiometry system. System is controlled by PC thought the instrumentality of special program.

Monochromator has few gratings with different number of lines per millimetre. The changing of ratings is not support of automatic regime. The replacement of gratings is

realized manually. Slits are not continuously adjusted. Their width can change also manually. The system has one input and output port. Communicating with MDP-41 is provided via the RS-232 interface.

This installation allowed to use two detectors. It is photomultiplier tubes (PMT) with different responsivity in various wavelength ranges. This decision provided a possibility to measure sequentially wide wavelength range. Firstly, UV area of wavelength range is researched then the IR area is available. Totally, installation allows to use wide wavelength range (200 - 1100 nm).

2.3 Distribution functions of defects and built-in charge in dielectric layer

The determination of built-in charge density distribution is not the primary purpose of this study, so this technique is shown below as a supplement. This technique is not considered in detail here.

When the study of formation and accumulation processes of luminescence centers in various EL bands is done, it is supposed that some expression for this process exists. This affirmation is held when the distribution of concentration through the thickness of oxide layer is defined.

One assumes that the dependence of EL intensity in certain band range on the thickness of dielectric layer $L(x)$ is described as a first approximation by the following expression:

$$L(x) = \int_0^{x_0} n(x) f(x) dx, \quad (2.1)$$

where x_0 is the oxide layer thickness; $n(x)$ is a concentration of luminescence centers at distance x from the semiconductor interface; and $f(x)$ is a function of excitation of luminescence centers.

The number of luminescence centers $N(x_0)$ is defined as

$$N(x_0) = \int_0^{x_0} n(x) dx. \quad (2.2)$$

Then, it is possible to get the information about formation and accumulation kinetics of these centers. In this case it is necessary to investigate the dependence of $L(x)$ during the layered growth. In addition it is needs to know the type of excitation function $f(x)$ for these EL centers.

It is possible to obtain the distribution profiles of EL centers through the thickness of oxide layer. For this purpose it is required to differentiate graphically the dependences of $L(x)$, which were obtained during layer-by-layer etching of dielectric layer. Also it is needed for the type of $f(x)$.

Since the preliminary data of spatial distribution of luminescence centers is known, it is simple to determine the type of excitation function of EL centers. Thus one can receive additional information about electrophysical parameters of studying structures.

To determine the profile distribution of built-in charge in dielectric layers the capacity-voltage characteristic of dielectric-semiconductors were measured. Measurements are held during the layer-by-layer etching of oxide layer. Using these characteristics the flat band voltages were determined.

2.4 Used samples and preparation's procedures to anodic oxidation

Monocrystalline silicon samples were used in the present study. The samples were oxidized using various techniques (thermal or anodic oxidation).

Silicon wafers (n-and p-type) were used as a substrate. The resistivity of this silicon type is 4 - 40 ohm·cm. The samples were cut in planes (100) and (111) and were subjected to preliminary mechanical, chemical and chemical-dynamical polishing.

The structures of Si-SiO₂^{thermic} were produced using thermal oxidation methods in an atmosphere of dry oxygen and in the atmosphere of dry oxygen with addition of HCl

vapors at the temperatures 1000 and 1100 °C. Thus, the thickness of silicon dioxide layer has varied in the range of 20 - 160 nm.

In a present study the samples described above were used. The samples were prepared beforehand and were taken from laboratory of microelectronics of Petrozavodsk State University.

Due to the fact that the properties of oxide films, and consequently the properties of silicon-silicon dioxide structures, which were obtained during anodic oxidation, essentially depend on the substrates (silicon) preprocessing.

Just before the anodic oxidation of the samples a chemical cleaning of its surface was carried out (standard treatment). This processing includes next steps:

1. Washing the sample in isopropyl alcohol, and mechanical cleaning the surface from dust pollution;
2. Boiling the sample in distilled water;
3. Washing the sample in isopropyl alcohol;

Procedures described above provided the removal of various organic and inorganic contaminations from the surface of the silicon plate.

4. Natural oxide layer removal by etching in acid. The 46 % solution of hydrofluoric acid was used in current study;
5. Washing the sample in distilled water in order to remove acid residual from the silicon layer;
6. Washing the sample in isopropyl alcohol to remove water;
7. Thorough drying.

Ohmic contact to the silicon substrate was made using indium-gallium eutectic. It was applied to mechanically pre-polished silicon surface.

Except some cases anodic oxidation of silicon was carried out in solution of 0.04 N KNO_3 in ethylene glycol with water content less than 2%. All measurements were made in the dark. In these purposes the carton shield (box) was created. In all cases, oxidation was carried out in a fresh electrolyte.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Experimental results

Figure 3.1 shows the EL spectra for the Si-SiO₂ structure. During the experiment characteristic bands of luminescence with energies 1.9, 2.3, 2.7, 3.3, 3.8 and 4.6 eV were found in the spectrum. These bands are linked to the presence of various defects in the oxide layer and in the border of Si-SiO₂ interphase [29]. These spectra were taken from experiment, which were made in St. Petersburg State University a few years ago.

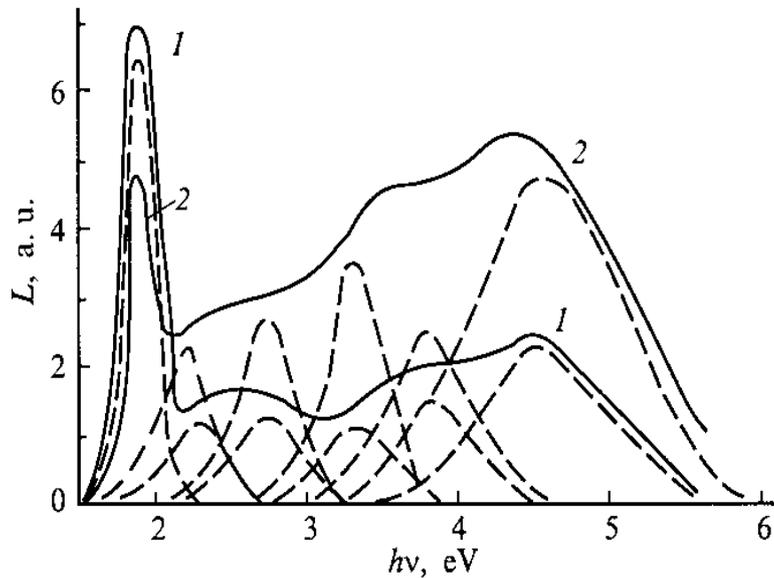


Fig. 3.1. EL spectra of standard Si-SiO₂ structures, which were obtained using thermal oxidation of silicon KDB-10 (100): 1 is an oxidation in water vapor at 950 °C, 2 is an oxidation in a dry oxygen at 1100 °C. [20]

It is shown that Si-OH groups, which are localized in the external layer of SiO₂, are the “red” luminescence centers (because of corresponding to infra red energy area). These centers are responsible for the EL in band with energy 1.9 eV.

The luminescence centers for energy band 2.3 eV on this graph is three-coordinated silicon, which is localized near the boundary of Si-SiO₂. Recorded EL spectra are explained by intracenter transitions in the atoms. Transitions exist because of the interaction of hot electrons in the oxide layer. Luminescence centers, which are responsible for EL in the ultraviolet (UV) spectral region, are located near the boundary of Si-SiO₂ [29]. Its nature for these structures has not been established yet.

In comparison with results which were obtained in Lappeenranta University of Technology the EL spectrum of Si-SiO₂ structures has an appearance such in Fig. 3.2. There is no band with energy 1.9 eV in this EL spectrum. It indicates that Si-OH groups are absence completely in the oxide layer. This is due to feature of pattern fabrication technique. The technique excludes a penetration of water fragments (hydrogen and hydroxyl groups) into oxide layer. The other suggestion is chemically very pure material (electrolyte), which contains almost no water molecular.

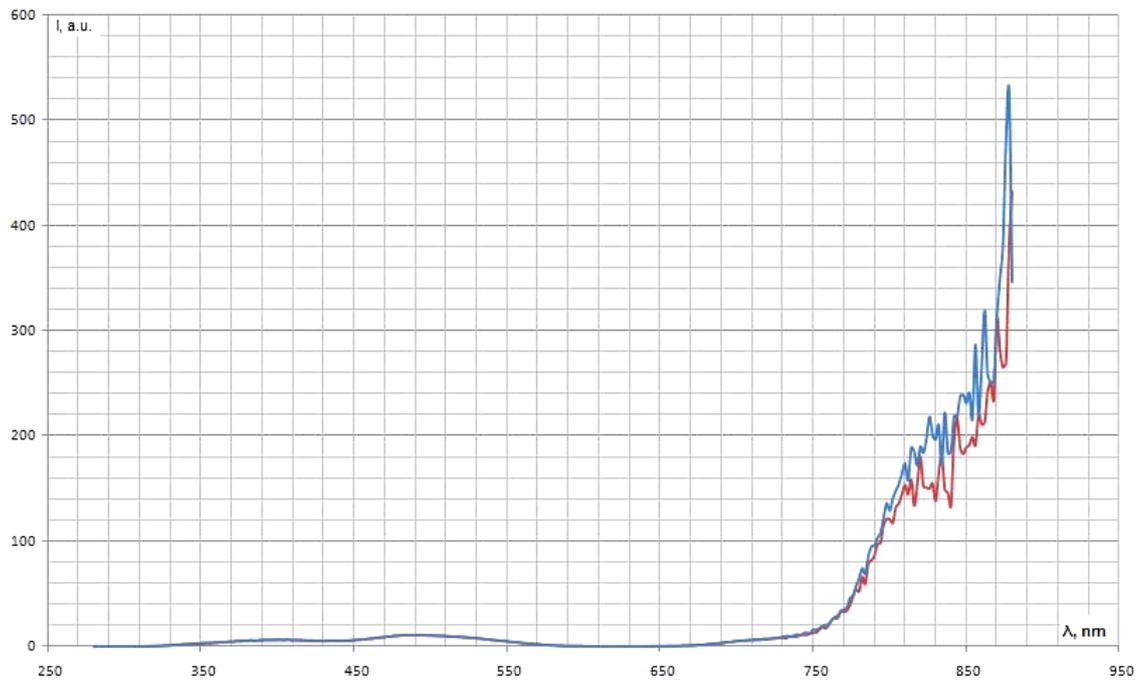


Fig. 3.2. EL spectra of Si-SiO₂ structure (intensity I [a. u.] versus wavelength λ [nm]). Formation was held in potentiostatic mode. End-point voltage for experiment 1 (red) and 2 (blue) is 272 V and 292 V, respectively.

Figures 3.3, 3.4 and 3.5 show the EL spectrum measured in Petrozavodsk State University. The band with energy 1.9 eV also is absent here. The samples were the same like in previous series of measurements in Lappeenranta University of Technology.

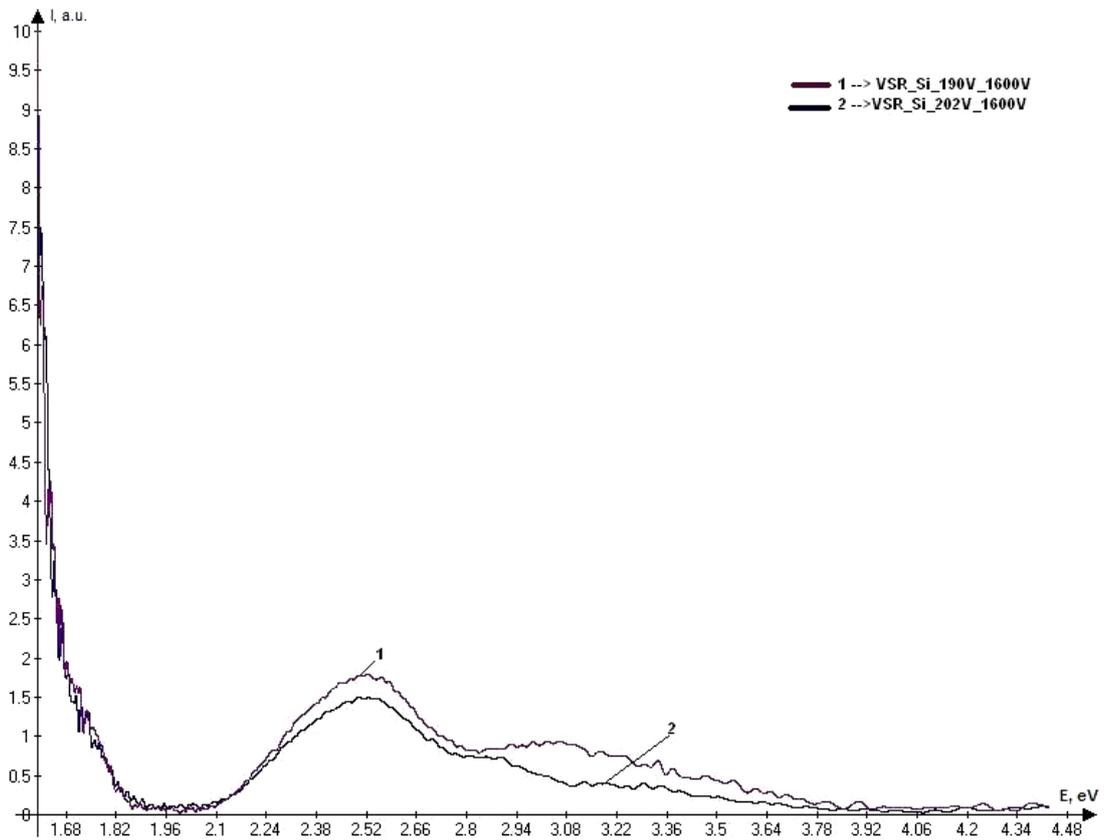


Fig. 3.3. EL spectra of Si-SiO₂ structure (intensity I [a. u.] versus energy E [eV]). Formation was held in potentiostatic mode. Different series of measurements have different magnitude of voltage.

It is possible to conclude that used samples almost don't contain water molecules and the electrolyte was chemically pure. Therefore nature of distribution of Si-OH groups in the oxide layer depends on the percentage of water content in the forming electrolyte. Increased water content in the electrolyte leads to shift of the maximum localization Si-OH groups to the outer edge of oxide layer. This leads to significant broadening localization region of hydroxyl groups.

Therefore, the less water in the electrolyte, the less expressed is the band 1.9 eV in spectrum.

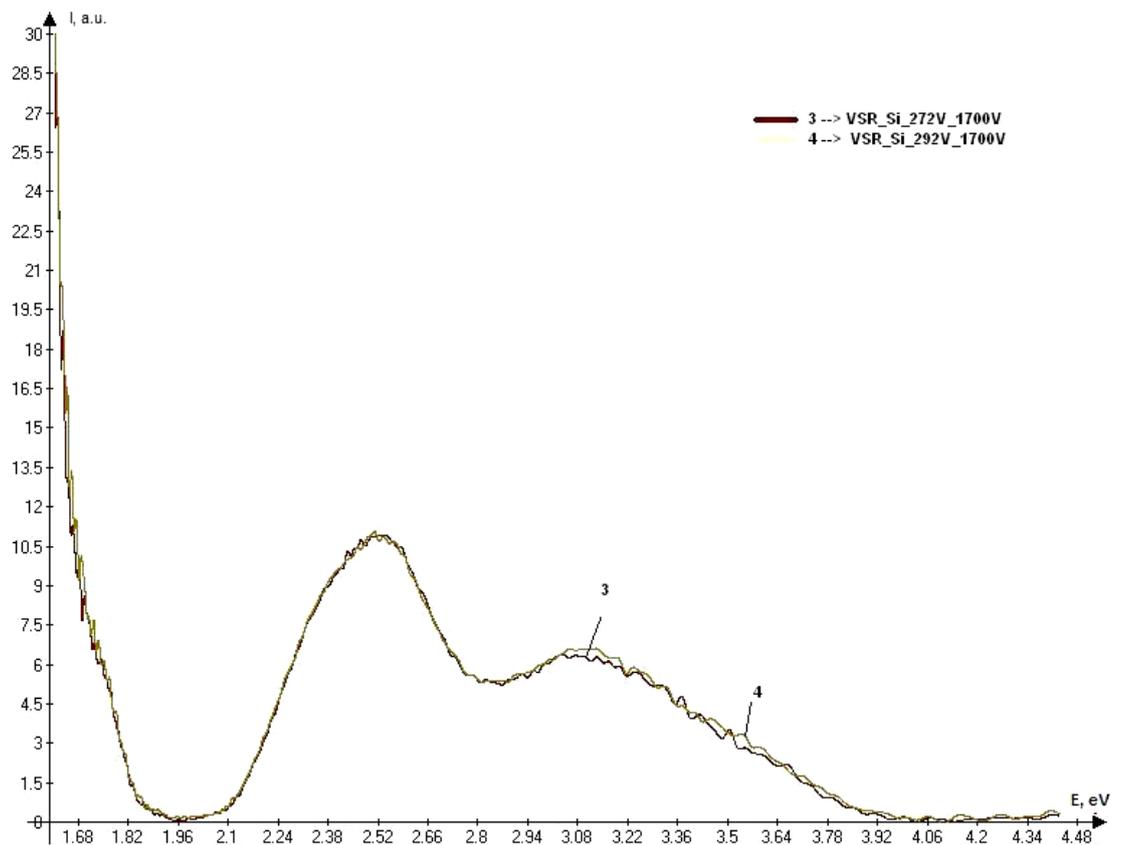


Fig. 3.4. EL spectra of Si-SiO₂ structure (intensity I [a. u.] versus energy E [eV]). Formation was held in potentiostatic mode. End-point voltage for experiment 3 and 4 is 272 V and 292 V, respectively.

Based on both current and prior results, it can be concluded that the anodic oxidation of silicon in galvanostatic regime can be divided at least into two phases. These stages are characterized by different mechanisms of oxide layer formation.

At the first stage anodic oxidation of silicon (forming of oxide layer to thickness of ~ 25 nm) holes are handed on in the formation of oxide layer. The increase of the concentration of holes in the surface area of silicon leads to an increase in speed of oxide's formation.

Defects, localized near the boundary of Si-SiO₂, are responsible for the initiation of EL in the 2.3 eV [12]. The studies showed that at the first stage of oxidation the intensity of the band 2.3 eV is reduced, i.e. concentration of defects of this type is felt (defect-type Si⁺ - dangling bond).

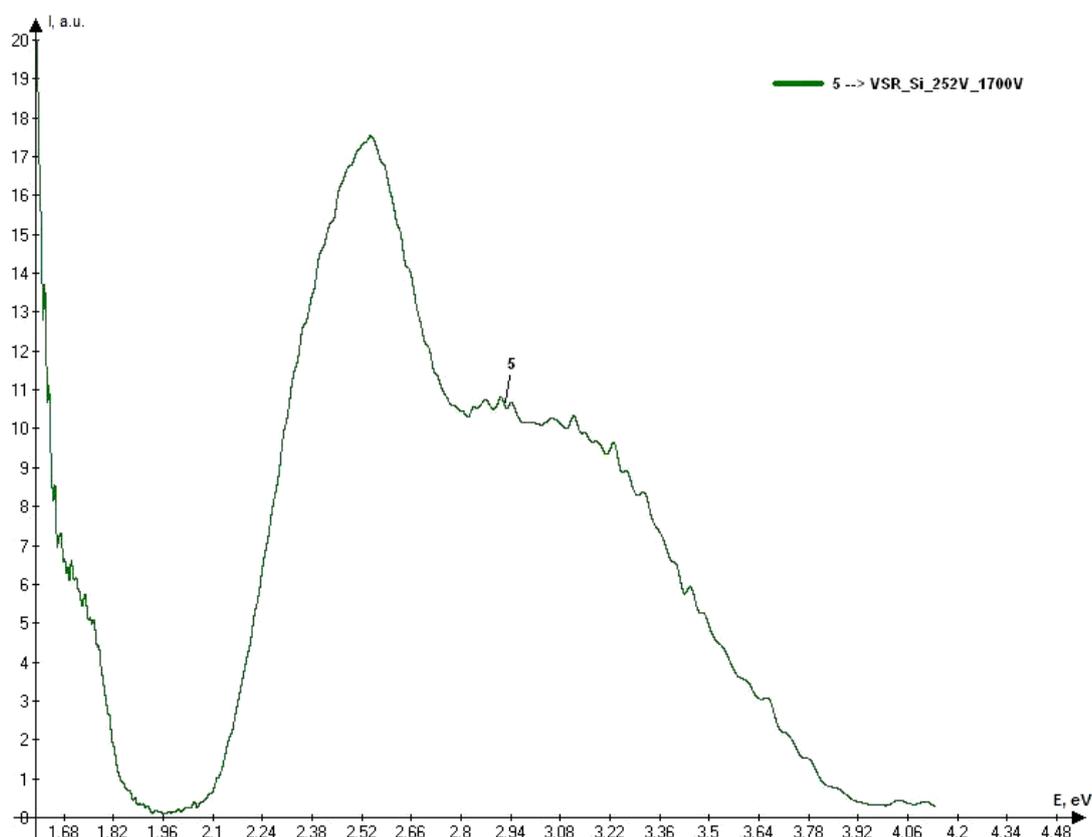


Fig. 3.5. Dependence of EL intensity [a. u.] on energy [eV]. Formation was held in potentiostatic mode. End-point voltage for experiment 5 is 252 V.

The transition from first formation mechanism to second begins when the oxide layer is reached the thickness 25 nm. Full transition to the second mechanism occurs when the thickness of oxide layer became more than 40 nm.

The second phase of the oxidation process is related to the development of impact ionization in the SiO_2 . This increase in oxide layer occurs at the boundary with the electrolyte due to the diffusion of silicon atoms under the influence of strong electric field.

Measurements of luminescence spectra in the process of anodic oxidation have been showed that, starting with oxide layer thickness such as 40 - 50 nm, redistribution of intensity in the ultraviolet part of the spectrum is observed. It is appears in alignment of relative intensity of peaks with energy 3.8 eV and 4.6 eV. It is possible to conclude the impact ionization in the SiO_2 at this phase of oxide layer formation is existed.

Luminescence spectra of the samples with subsequent forming completion in potentiostatic mode are shown in figures above. The intensity of fluorescence was proportional to the value of current density. This intensity was decreasing with the formation time. It should

be noted that in the final formation the phase intensity of luminescence band with energy 2.3 eV significantly decreased compared with the intensity of the other bands. It may be associated with formation completing of defects which have type Si^+ in the oxide layer.

In paper [28] electroluminescence in layers of thermal SiO_2 with thickness 34-130 nm was studied. Spectral distribution of EL presented a broad band radiation with a maximum at 2.5 eV. This peak is explained by means of presence the radiative recombination through the impurity states in a band gap of silicon dioxide.

3.2 List of results

1. Investigation of metal oxides yielded negative results. Electroluminescence did not appear in electrolytes (NaOH , H_2SO_4) which were used in this study, though the formation of oxides on metals was observed.
2. Several papers showed that the spectral distribution of EL for Si- SiO_2 structures in the range of wavelengths 250-800 nm consists of the six characteristic bands of radiation ($\sim 1.9, 2.3, 2.7, 3.3, 3.8$ and 4.6 eV).

Relative intensity of these bands depends on the composition and structure of oxide layer. This intensity is determined by the conditions of oxide layer formation.

3. It has a significant influence of electrons heating in oxide layer on the nature of electronic processes in Si- SiO_2 structures. The existence of two phases of heating in SiO_2 is shown. These phases have different channels of energy dissipation for hot electrons. In the first stage of heating the energy dissipation occurs through impact excitation of biographical defects in oxide layer and the interphase boundary of Si- SiO_2 . The relaxation of these excited defects into initial states is attended by the luminescence (it is the bands of EL: 2.3, 3.3, 3.8 and 4.6 eV).

The transition to the second stage occurs when the magnitude of electric field in oxide layer achieves the critical value E^* . It is associated with the development of impact ionization processes. Additional channel of energy dissipation for hot electrons start to

activate during these ionization processes. Energy dissipation channel depends on impact generation of electron-hole pairs in the oxide layer.

4. There is effect of intensity redistribution in the EL spectrum of Si-SiO₂ structures. It happens when the magnitude of electric field in oxide layer reaches the critical value. This effect argues about the redistribution of energy dissipation routes for hot electrons when transition from first to second stage of heating of electrons exists.
5. The unified mechanism of formation for negative charge was considered. This mechanism is associated with the transformation of Si-OH groups when Si-O* (asterisk here means a presence of one dangling bond) centers capture an electrons.
6. An active role of the current's electronic component for the anodic oxide layers formation processes was determined. Oxide formation process has at least two mechanisms. It is known that, transition to the second mechanism occurs regardless of the type of substrate and oxidation conditions. Main detail here is that the silicon oxide thickness should be no less than ~ 40 nm for starting transition. This transition could be explained via development of impact ionization process in a bulk of oxide layer.

Thus, the EIS system to study the insulator-semiconductor structures by EL technique is unique. In addition, it has several advantages over the MDS system with semitransparent metal electrodes.

In conclusion, it is necessary to note that the study of the electroluminescence spectral distribution in the EIS system allows to study a dielectric layers, to determine concentration of luminescence centers and its spatial distribution.

CONCLUSION

Important part of EL technique's development was using for measurements of EIS system. On the one hand, electrolyte has metal properties (injecting junction). At the same time, electrolyte has a number of specific features which expand resources of EL technique, i.e. improve method accuracy and informativity. Moreover, the main features of EIS systems used in the implementation of EL technique were described.

At first, here is the possibility to make significantly stronger electric fields in the dielectric layer in comparison with the metal-insulator-semiconductor (MIS) structures. These electric fields are homogeneous during the anodic polarization of the structures. It is necessary to apply positive voltage across the semiconductor in this case. Possibility to make stronger electric fields connects with the large potential barrier height for electrons at the interface of insulator-electrolyte (4.2 ± 0.2 eV for the SiO₂ border - aqueous electrolyte). Low injection ability of electrolytic contact blocks the breakdown of dielectric films in strong electric fields.

Secondly, electrolyte has high spectral transparency. Aqueous solution of sodium sulfate has losses less than 5% in the wavelength range 250 - 800 nm.

Third, there is ability to measure spectral distribution of EL both a layer-by-layer etching and layered growth of dielectric layer e.g., in the case of anodic oxidation of silicon.

Fourth, there is possibility to reduce significantly the effect of interference on the type of EL spectrum. In this connection semi-infinite field electrode is used, i.e. the electrode which geometric dimensions significantly exceed the wavelength of radiation. It is not possible when the semitransparent metal electrodes are used. It is impossible also to match the refractive index of electrolyte which will be the same like index of studied dielectric. These conditions allow to replace a multiple-beam interference by two-beam interference.

It is rather simply to change field electrode. Due to this, one has possibility to make a single measuring cycle with a various field electrodes (electrolytes). Electrolytes with different chemical compositions and refractive indexes can be used in determination of localization luminescent centers. There is also ability to influence pointedly on the investigated sample through the open outer border (doping out of the electrolyte).

Thus, the use of electroluminescence technique allows to investigate the Si-SiO₂ structures and receive information about their structural and electrophysical properties efficiently and quickly. Time for one spectrum is approximately 10 minutes.

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