PHYSICS OF SEMICONDUCTORS AND DIELECTRICS

PHYSICAL-CHEMICAL PROCESSES IN SILICON DIOXIDE FILMS EXPOSED TO STRONG ELECTRIC FIELDS

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The effect of strong electric fields exceeding $10^6$ V/cm on the metal – insulator – metal (MIM) and metal – insulator – semiconductor (MIS) structures on the basis of silicon dioxide films is discussed. The processes in the dielectric layers in the MIM and MIS structures are shown to be similar. These generate electrically active defects due to the action of hot electrons causing breakage of the weakened bonds Si–O, Si–H, and Si–OH. The defects generated are likely to be silicon atoms with the dangling bond $\equiv$Si$^\bullet$.

Silicon dioxide films (SiO$_2$) are widely used in microelectronics as one of the main dielectric materials. The MIM and MIS structures are often formed using a SiO$_2$ layer, whereas the Si–SiO$_2$ system makes the basis for integrated circuits for field-effect transistors. In most cases the dielectric films in the MIM and MIS structures work under strong electric fields exceeding $10^6$ V/cm. The stability of parameters of the devices based on these structures is largely determined by physical-chemical processes occurring in the dielectric layers. So far, little attention has been paid to the role of chemical processes. Furthermore, most studies of the MIS structures deal with the processes in semiconductors and at the Si–SiO$_2$ interface. The processes in dielectric films are shown to play a significant role in these structures [1]. In this connection, the investigation into the physical-chemical processes in silicon dioxide films exposed to strong electric fields is an important problem of scientific and practical interest.

In the present work, the results of experimental investigations into the influence of strong electric fields on the SiO$_2$ films are reported. On the basis of the experimental data, mechanisms responsible for the phenomena occurring in silicon dioxide films are proposed.

The Si(n-type)–SiO$_2$–M or MIM-structures with 20–200 nm thick dielectric layers were investigated. The SiO$_2$ films were produced by magnetron sputtering of a silicon target in the atmosphere of “dry” or “humid” oxygen. The static volt-ampere and high-frequency capacity–voltage characteristics of the structures were measured under constant voltage in the air and in vacuum. The properties of the films were analyzed by the Auger and IR-spectroscopy.

An irreversible increase in the steady leakage current is observed in the Mo–SiO$_2$–Al structures exposed to the electric field exceeding $10^6$ V/cm in vacuum higher than $10^{-2}$ mm Hg. For the specified electric fields, the volt-ampere characteristic of the steady leakage current in the MIS structure is linear in the Fowler–Nordheim coordinates suggesting the tunnel mechanism of conductivity [2]. The current through the structure and the density of the positive-charge formed in dielectric are shown in Fig. 1a and Fig. 1b versus the time of exposure to electric fields of different strengths. The positive-charge density was determined from the shifts of the static volt-ampere characteristics. In this method, a change in voltage resulting from exposure of the samples to strong electric fields is measured in the regime of direct current flowing through the sample (a positive potential in the direct polarity and a negative potential in the reversed polarity at the upper electrode are measured).

According to the techniques described in [3–5], the charge density $Q_D$ in a dielectric can be found from the following relation:
where \( \varepsilon \) is the relative static permittivity of the dielectric film, \( \varepsilon_0 \) is the electric constant, \( d_D \) is the thickness of the dielectric, and \( \bar{x} \) is the centroid of the charge captured by the film and defined as

\[
\bar{x} = \frac{1}{d_D} \left[ 1 - \frac{\Delta U_-}{\Delta U_+} \right]^{-1},
\]

where \( \Delta U_- \) and \( \Delta U_+ \) are the voltage shifts, provided the volt-ampere characteristics of MIM structures are measured in the direct \( |\Delta U_+| \) and reversed \( |\Delta U_-| \) polarity, respectively, under constant current flowing through the structure

\[
\Delta U = |\Delta U_-| + |\Delta U_+|.
\]

The changes in the character of steady leakage current correlate well with the positive-charge density in the dielectric. This allows us to assume that the increase in the current with exposure time is connected with an increase in the electric-field strength in the vicinity of the cathode due to formation of a positive charge in the dioxide layer. The nature of the positive charge is likely to be due to formation of charged defects in the dielectric under the influence of hot electrons, strong evidence of their presence in the MIM structures was provided in [6]. The most likely process is the formation of positively charged defects in the SiO\(_2\) layer in the form of three-coordinated silicon due to the breakage of the weakest Si–H bonds and deformed Si–O and Si–OH bonds caused by hot electrons [6]. This assumption is supported by the fact that silicon dioxide films produced in the atmosphere of “dry” and “humid” oxygen differ by the number of Si–H- and Si–OH-bonds, according to the IR spectroscopic data.

On the assumption that the process of irreversible changes in the silicon dioxide under exposure to electric fields exceeding \( 10^6 \) V/cm is due to the breakage of the deformed Si–O bonds (among other bonds), the impurity atoms introduced into the dielectric layer should accelerate this process. We examined the Mo–SiO\(_2\)+Cu–Al structures where copper impurity was introduced into the silicon dioxide film during its deposition. The current dependences on the time of exposure of these structures to the electric field \( 10^6 \) V/cm are shown in Fig. 2a for various copper concentrations (in relative units). It is seen from the figure that the rate of current rise depends on the impurity concentration. Similar results are obtained for other metal impurity atoms (for example, Al) introduced into the silicon dioxide films (Fig. 2b). However, the quantitative parameters of the process depend on the type of metal impurity incorporated in the dielectric film. Thus, the effect of silver