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Crystallization processes of oxide films on the metal/oxide surface

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The paper presents the results of studies of thermal crystallization of oxide dielectrics Nb_2O_5 and Ta_2O_5. It was established that the dissolution of oxygen in niobium and tantalum contributes to the suppression of the degradation process associated with the reduction of amorphous oxide with a base metal. It is shown that as a result of redox reactions at the interfacial boundaries of the layered structure, oxygen from the oxide diffuses into the metal, oxidizing the latter. The oxide itself is reduced, which leads to local violations of the chemical composition of the oxide.

Keywords: niobium, tantalum, degradation, oxide dielectric, crystallization.

Представлены результаты исследований термической кристаллизации оксидных диэлектриков Nb_2O_5 и Ta_2O_5. Установлено, что растворение кислорода в ниобии и тантале способствует подавлению деградационного процесса, связанного с восстановлением аморфного оксида базовым металлом. Показано, что в результате окислительно-восстановительных реакций на межфазных границах слоистой структуры кислород из оксида диффундирует в металл, окисляя последний. Сам оксид при этом восстанавливается, что приводит к локальным нарушениям химического состава оксида.

Процеси кристалізації окисних плівок на поверхні метал/оксид. *І.Ш.Невлюдов, В.Н.Гурін, Д.В.Гурін, Ю.М.Олександров.*

Представлено результати досліджень термічної кристалізації оксидних діелектриків Nb_2O_5 і Ta_2O_5. Встановлено, що розчинення кисню у ніобії і танталі сприяє пригніченню процесу деградації, пов'язаного з відновленням аморфного оксиду базовим металом. Показано, що у результаті окисно-відновних реакцій на міжфазних межах шаруватої структури кисень з оксиду дифундує у метал, окислюючи останній. Сам оксид при цьому відновлюється, що призводить до локальних порушень хімічного складу оксиду.

The basis of the elemental base of radio electronics is made up of various devices based on metal-insulator-semiconductor structures (MIS structures). One of these elements are oxide-semiconductor capacitors (OSC) which are widely used in electronic equipment due to the optimal combination of their electrical parameters with overall dimensions, as well as due to an acceptable pricing policy [1–4].

Of particular interest is the mechanism for the degradation of defense sector equipment, which leads to operational failures. The identification of this mechanism is relevant to ensure the uptime of the defense sector. The study of the properties of oxide-semiconductor capacitors is based on modeling the processes in flat layered structures $Me(O)/a–Me_2O_5$ [5]. The methodology of such studies is described in detail in [6].

The thermal crystallization of the oxide dielectric of the $Me(O)/Me_2O_5$ layer with a different concentration of oxygen in the base metal was studied by optical observations of the $a–Me_2O_5$ surface using a light polarizer. Figure 1 shows micrographs of

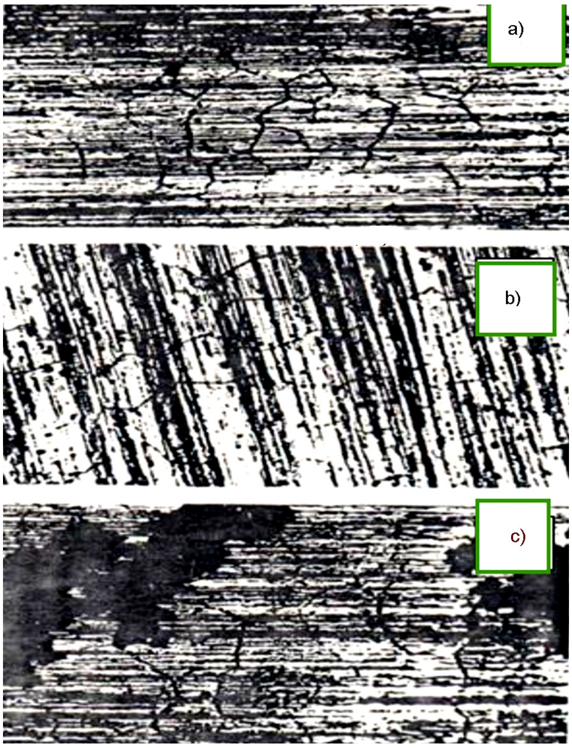

Fig. 1. Crystallization of a–$\mathrm{Me_2O_5}$ during annealing of layered Me/a–$\mathrm{Me_2O_5}$ structure with different oxygen content in metal: A — 0.05 at.%, B — 0.20 at.%, C — 1.60 at.%.

the a–$\mathrm{Nb_2O_5}$ film grown on the surface of niobium with an oxygen contents of 0.05 at.% (A), 0.2 at.%,(B), 1.6 at.% (C); the film was subjected to annealing in air at T = 800 K. As can be seen from Fig. 1, with an increase in the oxygen content in the base metal, the amount of precipitates of the crystalline phase in the amorphous matrix increases significantly, although the oxygen concentration in all cases remains below the limit of oxygen solubility in niobium. A similar situation is observed in layered structures based on a solid solution of oxygen in tantalum.

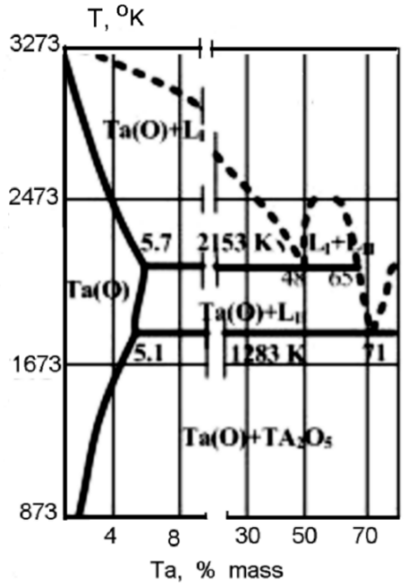

Fig. 2. Equilibrium diagram of the system Ta–O.

The reason for the decrease in the stability of the amorphous state of a–$\mathrm{Me_2O_5}$ films in the presence of oxygen in the base metal is the heterogeneity of the structure and chemical composition of the base metal. It is known [7] that in oxygen-containing niobium and tantalum there are domains with a high oxygen content, as well as inclusions of oxide and suboxide phases with an average volume concentration of oxygen significantly lower than its solubility in this metal. Such domains and inclusions, as a rule, are formed at the stage of cooling the samples after high-temperature doping with oxygen and are localized at the boundaries of the crystal grains of the metal, dislocations, some substitutional impurities, etc. The place of the increased oxygen content is also the surface area of the metal. Since the growth of the $\mathrm{Me_2O_5}$ film during the anodic oxidation of metals partly takes place deep into the metallic substrate [8], the inclusions located near the surface of the metal fall into the bulk of the oxide film. Such inclusions are effective centers of crystallization of an amorphous dielectric and cause its accelerated crystallization. Thus, the presence of oxygen in the base metal of the layered Me(O)/a–$\mathrm{Me_2O_5}$ structures has not an unambiguous impact on the degradation processes occurring in them. On the one hand, the presence of oxygen in the base metal causes an increase in the energy barrier for oxygen at the Me(O)/a–$\mathrm{Me_2O_5}$ interface to decrease the oxygen flow from $\mathrm{Me_2O_5}$ to Me(O); as a result, the stability of layered structures to degradation associated with partial restoration of the a–$\mathrm{Me_2O_5}$ film of the base metal increases. This result is consistent with the corresponding equilibrium diagrams of the Ta–O (Fig. 2) and Nb–O (Fig. 3) systems, according to which the oxygen saturation of the metal shifts the pair Me(O)/a–$\mathrm{Me_2O_5}$ towards a greater thermodynamic equilibrium. On the other hand, the presence of oxygen in the base metal causes a decrease in the stability of the amorphous state of a–$\mathrm{Me_2O_5}$ films due to the appearance of inclu-

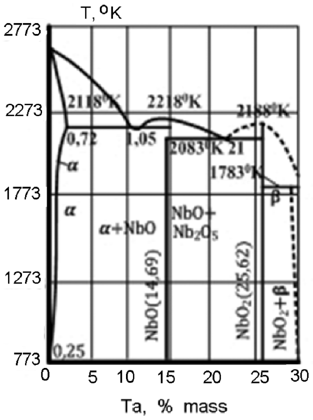

Fig. 3. Equilibrium diagram of the Nb–O system. Nb–O system.

sions of crystalline oxide phases already at the stage of growing the amorphous oxides.

Degradation processes consist in the course of redox reactions at the interface of the contacting phases. These reactions are due to the lack of thermodynamic equilibrium between them. As a result of the oxidation-reduction reactions at the interfacial boundaries of the layered structure, oxygen from the oxide diffuses into the metal, oxidizing the latter. The oxide itself is reduced. This leads to local violations of the chemical composition of the oxide, that is, to the appearance of oxygen "vacancies" which move to the oxide-semiconductor interface (in MIS structures) under the action of the chemical potential gradient. Since oxygen diffuses through the layered structure in the form of ions, the movement of the oxygen "vacancies" can be considered as a current of oxygen ions through the volume of the dielectric. When the vacancies reach the $a\text{–}Me_2O_5/MnO_2$ interface, they are filled due to the extraction of oxygen from the semiconductor; this causes structural transformations in the thinnest manganese oxide bordering the dielectric [9, 10].

Conclusions

The dissolution of oxygen in niobium and tantalum contributes to the suppression of the degradation process associated with the reduction of amorphous oxide with a base metal. This is due to a decrease in the chemical potential of oxygen and an increase in the energy barrier for oxygen at the boundary of $Me(O)/a\text{–}Me_2O_5$ compared to the $Me/a\text{–}Me_2O_5$ boundary. At the same time, the degradation processes associated with the crystallization of the amorphous phase are intensified. The result obtained gives grounds to improve the technological process of manufacturing the OSC by doping the initial structure with oxygen, which might improve the operational reliability of capacitors.

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