Specific features of production technology of stable niobium bilayers for capacitors

V.V.Starikov

Kharkiv State Polytechnical University,
21 Frunze St., 61002, Kharkiv, Ukraine

Study results of degradation processes in layer systems including bilayers $Nb–Nb_2O_5$ are presented for cases when the base metal contained various gas impurities. The possibilities of niobium refining from oxygen for amorphous state stabilization of the oxide layer formed on the metal surface are analyzed. The durability data of layer systems containing bilayers $Nb–Nb_2O_5$ on the base nitrogen-doped metal are discussed.

В статье представлены результаты исследования деградационных процессов в слоистых системах, включающих двухслойники $Nb–Nb_2O_5$, когда базовый металл содержал различные газовые примеси. Анализируются возможности очистки ниобия от кислорода для стабилизации аморфного состояния оксидного слоя, сформированного на поверхности металла. Обсуждаются результаты исследований долговечности слоистых систем, содержащих двухслойники $Nb–Nb_2O_5$ на основе легированного азотом металла.

1. Introduction

Bilayers composed of niobium and amorphous niobium pentoxide Nb_2O_5 as well as $Ta–Ta_2O_5$ bilayers are widely used in electronics as part of various solid state devices [1]. If the metal is niobium sintered powder and the external electrode is the semiconductor layer of manganese dioxide MnO_2, these trilayer systems $Nb–Nb_2O_5–MnO_2$ are the base of oxide-semiconductor capacitors with bulk-porous anode having a high specific capacity and also wider frequency and temperature operating ranges in comparison with other types of polar capacitors.

Despite of similarity of niobium and tantalum properties, it is just the oxide-semiconductor capacitors on the base of tantalum layer system that are mainly in production in the world, though niobium is both cheaper and lighter metal; moreover, the specific capacity of niobium capacitors is higher due to a favorable dielectric constant value of niobium pentoxide as compared to that of tantalum pentoxide [2]. The tantalum capacitors have been found to exhibit a greater reliability and durability than niobium ones. Such difference of tantalum and niobium capacitors is explained by difference in degradation processes rates proceeding in layer systems of both types.

The study of degradation in a system based on pure niobium has shown that the nature of this process is associated with thermodynamic instability of that system. Relaxation of the bilayer into a more thermodynamically stable state occurs through redox chemical reaction at the Nb/Nb_2O_5 interface, where oxygen from Nb_2O_5 is dissolved in Nb as well as through ordering and crystallization of the amorphous Nb_2O_5 film [3].

In real electronic components, niobium, especially if the metal is used as a powder, contains various impurities, which influence essentially the properties of niobium and niobium pentoxide on the metal surface [4]. So, it was experimentally confirmed that it is possible to reduce the degradation rate by doping of metal with nitrogen before its oxidation [5]. This approach may be effective for making electronic devices of

higher reliability and service duration. But the most active interstitial impurity in niobium is oxygen, which is characterized by the maximum heat of dissolution as compared to other typical interstitial impurities (nitrogen, carbon, hydrogen) [6]. The presence of oxygen in the base metal can change the degradation rate and result in a reduced nitrogen solubility in niobium. The study of these phenomena is the aim of the present work.

2. Sample preparation and experimental techniques

The base metal of bilayer systems was prepared as a foil (for model samples) and sintered powders (for oxide-semiconductor capacitors). Niobium foils and powder contained impurities in amounts of (in ppm): Ta,<800; Fe,<70; Si,<70; Ti,<80; W,<80; C,<100; O,<300; N,<100; H,<10. Niobium foil was annealed for t = 30 min at T = 2100 K in vacuum P = 8·10^{-4} Pa. Niobium powder was sintered into porous tablets for t = 30 min at T = 2100 K and P = 8·10^{-4} Pa.

Dissolution of oxygen in the niobium foil was realized due to the sample exposition for different time intervals in oxygen atmosphere at T = 1950 K and P = 2·10^{-3} Pa. Niobium foils and porous tablets were doped with nitrogen by annealing at T = 1470–1520 K in vacuum chamber filled with nitrogen at the pressure P = 2·10^{-1} Pa.

The chemical composition of foils and bulk-porous anodes was controlled by laser and secondary-ion mass-spectrometry (LMS and SIMS) methods. A laser with a power of 10^{13}–10^{14} Wt/m^2 and the pulse duration 10–20 ns was used for LMS. Argon ions of 3–5 keV energy were used for SIMS. Besides, the period crystal lattice (a) and microhardness (HV) of foils were determined. The value of a was determined by X-ray analysis with cobalt K_α radiation. HV was determined by the Vickers method using a load of 0.1 kg.

The Nb$_2$O$_5$ film of a thickness h = 1·10^{-7} m was grown on the niobium by electrochemical oxidation in 0.01 M aqueous solution of phosphoric acid at room temperature and had the stoichiometric composition. The second electrodes were 0.01 M aqueous solution of acetic acid or semiconductor manganese dioxide.

The heat treatment for redox reaction stimulation at the Me/Me$_2$O$_5$ boundary was performed at T = 525 K and P = 2·10^{-4} Pa

during 60 min. The parameter characterizing the extent of degradation was the relative increase of electrical capacity, $(C-C_0)/C_0$, of the layer system Nb–Nb$_2$O$_5$-electrolyte after annealing of the Nb–Nb$_2$O$_5$ bilayer in comparison with unannealed ones. According to [7, 8], the electrical capacity increase is connected with decrease of the efficient thickness h and increase of the dielectrical constant ε of Nb$_2$O$_5$ resulting from interaction between metal and oxide under annealing that caused an oxygen deficiency in Nb$_2$O$_5$ films. If the external electrode is MnO$_2$, the trilayer system Nb–Nb$_2$O$_5$–MnO$_2$ under heating at the same temperature displays the properties of a galvanic cell [7] and the temperature 525 K corresponds to the conditions of the maximum output power generated by niobium trilayer. The properties of galvanic cells allow to determine the electrical parameters characterizing the degradation processes. The current of oxygen ions was determined experimentally as the short-circuit current I_{sc} in the circuit composed of a heated sample and a galvanometer. The activation energy of ion conduction, W, was calculated from the temperature dependence $I_{sc}(T)$ as the plot slope in the $\ln I_{sc}$–T^{-1} coordinates. The conductivity of Nb$_2$O$_5$ film was measured under the positive polarization of the base metal at room temperature and at a voltage corresponding to the ohmic area of the IU characteristic.

3. Results and discussion

Dissolution of oxygen in niobium results in the displacement of tantalum, that is main substitution impurity, towards the foil surface and oxygen concentration in the foil volume exceeds one near the foil surface [9]. The enrichment of boundary Nb(O)/Nb$_2$O$_5$ in tantalum is a specific feature of the system under study, which is to take into account when considering the degradation mechanism of Nb–Nb$_2$O$_5$ bilayer.

The dependence of microhardness (HV) (curve 1) and the crystal lattice period (a) of Nb(O) solid solution (curve 2) as well as of relative increase of the electrical capacity $(C-C_0)/C_0$ for layer system (curve 3) upon the oxygen concentration in niobium are displayed in Fig.1. It is seen that with increasing oxygen concentration, a monotonous decrease of $(C-C_0)/C_0$ and increase of HV and a are observed. The saturation of all parameters occurs at oxygen concentration 2.2 at.% close to its solubility limit in
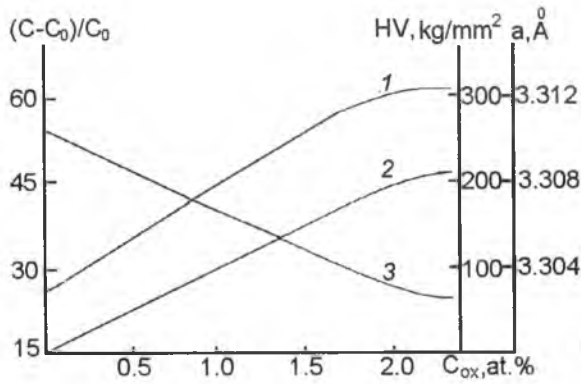
Fig.1. The dependences of microhardness (1), crystal lattice parameter (2), and $(C-C_0)/C_0$ ratio (3) on oxygen concentration in the base metal for flat model $Nb(O)-Nb_2O_5$ bilayer.

niobium [6]. The stabilization of C with increase of the oxygen contents in the base metal is associated with the delay of redox reaction at the metal-amorphous oxide interface. Monotonous character of $(C-C_0)/C_0$ change evidences that it is just the interface that plays a limiting art in the oxygen transfer across the $Nb(O)-Nb_2O_5$ system at any oxygen concentration in $Nb(O)$.

The measurements of activation energy, W, of oxygen ion transport across the layer system have shown that W grows from $W = 1.52$ eV for system on the base of pure niobium to $W = 1.68$ eV for that on the base of $Nb(O)$ where oxygen concentration is close to solubility limit in niobium at room temperature. This changing of W can be associated with the gradual increase of the energy barrier height for oxygen on the $Nb(O)-Nb_2O_5$ interface due to both niobium saturation in oxygen and the interface enrichment in tantalum.

Thermal crystallization of amorphous oxide of bilayer $Nb(O)-Nb_2O_5$ at different oxygen concentrations in the base metal was studied by optical supervision of the Nb_2O_5 surface using a light polarizator. It is established that at the increase of the oxygen content, in the base metal, the number of the crystal phase inclusions in amorphous matrix grows considerably, though the oxygen concentration in all cases remains below the oxygen solubility limit in niobium at $T = 300$ K.

The structure heterogeneity and chemical composition of base metal are the reasons of amorphous state stability decrease in Nb_2O_5 film due to oxygen presence in the base metal. If niobium contains oxygen, there are domains with the increased oxygen concentration and also the inclusions of oxide and suboxide phases while the average volume oxygen concentration is much lower than the oxygen solubility limit in the metal [10]. As a rule, such domains and inclusions are formed at the sample cooling stage after high-temperature doping with oxygen and are located at boundaries of metal crystal grains, dislocations, some substitution impurities, etc. The metal region adjacent to the surface is the contains an increased oxygen amount, too. As the growth of Nb_2O_5 film by anodic oxidation of metal partially occurs into depth of metal [2], the inclusions located near to the metal surface get into the oxide film volume. Such inclusions are effective crystallization centres of amorphous dielectric and accelerate this process.

Thus, the presence of oxygen in the base metal of bilayers influences degradation processes proceeding therein in two ways. On the one hand, the presence of oxygen in the base metal causes an increase of the energy barrier height for oxygen at the Nb/Nb_2O_5 interface, reduction of oxygen transfer from Nb_2O_5 to $Nb(O)$ and, hence, increases the stability of the layer system against degradation associated with partial reduction of Nb_2O_5 film by the base metal. This result is in agreement with the corresponding equilibrium diagram of $Nb-O$ system [6], according to which the metal saturation with oxygen displaces the Nb/Nb_2O_5 couple to closer to the equilibrium state. On the other hand, the presence of oxygen in the base metal causes a decreased stability of Nb_2O_5 film amorphous state in connection with occurrence of crystal oxide phase inclusions already at the stage of amorphous oxide formation. Thus, the problem of preliminary cleaning of base metal from oxygen before formation of bilayer $Nb-Nb_2O_5$ is of considerable importance.

The refining of niobium and tantalum from oxide phases is possible by means of vacuum annealing at $T > 2000$ K [6]. If the oxygen concentration in niobium exceeds its solubility limit at room temperature, the cleaning of metal is possible by heat treatment at elevated temperature due to tantalum impurity redistribution in niobium and formation of diffusion barrier for oxygen. Such a cleaning technology is acceptable, however, for compact metal only, while in the case of bulk-porous anodes sintering for oxide-semiconductor capacitors from a metal powder, becomes their specific capacity sharply reduced because of decrease of

the free anode surface area. Other possible ways to the metal refining consist in the use of carbon and hydrogen.

The use of carbon allows clean niobium effectively to at lower annealing temperatures ($T \sim 1700$ K). However, even an insignificant overdose of carbon dissolved in metal results in formation of small carbide phase amounts on niobium surface that worsens quality of oxide films formed on the surface by anodic oxidation because of increase in its conductivity [11].

Purification of niobium from impurities using hydrogen begins already at the hydrogen content in the metal $\sim 4 \cdot 10^4$ ppm at $T = 1000$ K. Use of hydrogen in the form of niobium hydride NbH_x powder (where $x = 0.7-1.0$) is more efficient. It is established experimentally, that such technology of porous anodes preparation for oxide-semiconductor capacitors provides a significantly decreased interstitial impurity concentration in the metal: carbon and nitrogen, by 10 times; oxygen, approximately by 2–3 times. The hydrogen concentration in the metal also drops sharply during the anodic tablet sintering, so the final hydrogen content in niobium does not exceed 10–30 ppm. The important fact is also that the impurity removal from the metal using hydrogen is not accompanied by absorption of carbon and oxygen from the vacuum furnace operating chamber that it is possible to explain by structural transformations of niobium crystal lattice during dissolution of hydrogen. Use of hydride powder for sintering of anodes of oxide-semiconductor capacitors opens a way to application of fine powders (up to diameter 10^{-5} m) at a sufficiently high degree of their purification, that will allow to increase essentially the specific capacity of niobium capacitors.

The offered technology of niobium powder purification from oxygen allows to prepare layer systems on the niobium base having increased stability, since the reduction of oxygen concentration in the metal facilitates dissolution of nitrogen therein. The nitrogen concentration in the metal for doping of bulk-porous anodes of trilayer capacitor systems is chosen using earlier results for plane bilayers models [12]. Durability of trilayer system containing nitrogen-doped metal, $Nb(N)-Nb_2O_5-MnO_2$, in comparison with a similar one on the base of pure metal $Nb-Nb_2O_5-MnO_2$ was studied while functioning of samples as galvanic cells. The experimental dependences of electronic con-
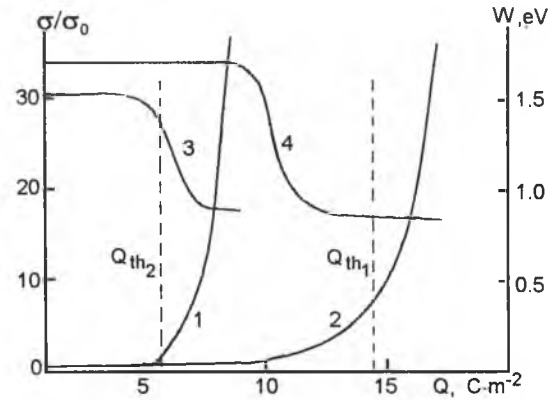

Fig.2. The $\sigma(Q)$ (1,2) and $W(Q)$ (3.4) dependences for $Nb-Nb_2O_5-MnO_2$ (1,3) and $Nb(N)-Nb_2O_5-MnO_2$ (2,4) capacitor trilayers with bulk-porous anode.

ductivity change σ, of trilayers and activation energy W of oxygen ion conductivity are presented in Fig.2. The total charge Q of oxygen ions flowing under heating across Nb_2O_5 from MnO_2 to Nb is the integral degradation extent which characterizes the actual age of a trilayer. The value of this charge is calculated as the integral of short-circuit current on the experiment time. Dissolution of nitrogen in the metal is accompanied by an increase of the activation energy of oxygen ion transport W across the $Nb-Nb_2O_5-MnO_2$ layer system from 1.52 eV in the trilayer on the base of pure metal to 1.65 eV in that based on doped metal when the nitrogen concentration in the metal is near to the nitrogen solubility limit at room temperature. The degradation suppresion is connected with both the decrease of oxygen transfer rate across the trilayer and the increase of activation energy of this process. Dissolution of nitrogen in the metal prior to its oxidation turned out to increase more than twice the life time of the niobium-based layer system functioning as a capacitor system. Thus, the nitrogen forms the barrier against oxygen and this barrier effect causes the stabilization of chemical composition and electrical properties of the studied layer systems.

The present work has shown that at low concentration of oxygen in the base metal the degradation rate of $Nb(O)-Nb_2O_5$ bilayer depends on the redox reaction rate at the metal-oxide interface. As the oxygen concentration in niobium increases, the redox reaction rate decreases but the probability of occurrence of crystal inclusions into amorphous oxide film increases already at

the stage of oxide formation that causes a sharp increase of degradation rate associated with crystallization of the amorphous oxide. The enrichment of Nb(O) the surface in tantalum accelerates even more the degradation because the layer system based on triple solid solution (Nb,Ta) (O) is thermodynamically less stable than the system on the base of its binary analogue Nb(O). The dissolution of nitrogen in Nb reduces the degradation rate of Nb–Nb$_2$O$_5$ bilayer, thus providing increased reliability and life time of electronic devices made on its base. Preliminary purification of metal enhances further the positive effect of nitrogen doping on the structure stability and properties of metal-oxide bilayers and, hence, increases the reliability and life time of electronic components based on such layer systems.

References

1. N.F.Jackson, D.L.Campbell, *Thin Solid Films*, **36**, 331 (1976).

2. L.Young, Anodic Oxide Films, New York, Academic Press (1961).

3. B.T.Boiko, V.R.Kopach, S.M.Melentyev et al., *Thin Solid Films*, **229**, 207 (1993).

4. N.Shamir, U.Atzmony, *J. Vac. Sci. Technol.*, **5**, 1024 (1987).

5. T.Kamei, E.Matsuraki, *Thin Solid Films*, **77**, 259 (1981).

6. E.Fromm, E.Gebhardt, Gase und Kohlenstoff in Metallen, Springer Berlin (1976).

7. D.M.Smith, G.A.Shirn, T.B.Tripp, *J. Electrochem. Soc.*, **110**, 1271 (1963).

8. H.Oechsner, J.Giber, *Thin Solid Films*, **24**, 199 (1985).

9. Yu.L.Pozdeev-Freeman, M.N.Naboka, V.V.Starikov, *Cryst. Res. Technol.*, **30**, 329 (1995).

10. L.L.Odynets, V.M.Orlov, Anodic Oxide Films, Leningrad, Nauka (1990) [in Russian].

11. V.V.Starikov, L.N.Lykov, *Cryst. Res. Technol.*, **31**, 917 (1996).

12. A.I.Fedorenko, V.V.Starikov, Yu.L.Pozdeev, I.N.Lykov, *Cryst. Res. Technol.*, **32**, 843 (1997).

Особливості технології виготовлення стабільних ніобієвих двошаровиків для конденсаторів

В.В.Старіков

У статті подано результати дослідження деградаційних процесів у шарових системах, що включають двошаровики Nb–Nb$_2$O$_5$, коли базовий метал містить різноманітні газові домішки. Аналізуються можливості очистки ніобію від кисню для стабілізації аморфного стану оксидного шару, сформованого на поверхні металу. Обговорюються результати досліджень довговічності шарових систем, що містять двошаровики Nb–Nb$_2$O$_5$ на основі легованого азотом металу.