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Layer Systems on the Base of Nitrogen-Doped Tantalum and Niobium with Enhanced Stability

There are presented the results of the investigation of tantalum- and niobium-based metal-oxide bilayers degration in dependence on chemical composition of base metal. Nitrogen dissolved in metal increases stability of chemical composition and electrical properties of oxide films grown on the metal surface by anodic oxidation. This improves reliability and life time of electronic devices containing tantalum- or niobium-based layer systems. The best positive effect of doping tantalum and niobium by nitrogen was achieved after preliminary refining of these metals from oxygen. When nitrogen concentration in the base metal essentialy exceeds its solubility limit at room temperature and nitride phases are formed the dielectrical properties of oxide film get worsen.

1. Introduction

Bilayers composed of a metal (Ta, Nb) and an amorphous dielectric film (Ta_2O_5, Nb_2O_5) are widely used in electronics as parts of various solid state devices [JACKSON, CAMPBELL]. It is well known [SMITH et al.] that the dielectric properties of the Ta_2O_5, (Nb_2O_5) layer in the metal-oxide bilayers are deteriorated in the course of time, either spontaneously or under the influence of an external electrical field. This leads to failures of the components of electronic circuits containing tantalum- or niobium-based bilayers.

The investigation of this phenomena showed [BOIKO et al. 1993] that the degradation nature is connected with thermodynamically non-equilibrium state of the $Me-Me_2O_5$ bilayers. The relaxation of bilayers into more thermodynamically stable state occurs through chemical redox reaction at the Me/Me_2O_5 interface, during which oxygen from Me_2O_5 dissolves in Me, and through ordering and crystallization of the amorphous Me_2O_5 film. Kinetics of these processe depend on type of the base metal [BOIKO et al. 1993].

According to the corresponding Me–O equilibrium diagrams [FROMM, GEBHARDT], the dissolving oxygen in the tantalum and niobium before oxidation approaches the pair Me and Me_2O_5 to the more thermodynamically equilibrium state. However, this approach to more stable metal-oxide composition isn't perspective because it leads to the essential activation of degradation processes connected with crystallization of amorphous oxides [PALATNIK, NABOKA et al. 1994; PALATNIK, et al. 1994].

Changing the bilayer construction, for example, at the expense of contact of oxide with other metal [BOIKO et al. 1985] was another approach to more stable metal-oxide systems. If the oxide is grown by anodic oxidation of tantalum or niobium as in the case of electrolytic capacitors the thremodynamical equilibrium can not be reached in principle. Therefore for such objects the decrease of degradation rate can be good alternative. Both the oxygen diffusivities rate can be good alternative. Both the oxygen diffusivities in the oxide and metallic layers and the rate of redox reaction at the interface boundary Me/Me_2O_5 determine the degradation kinetics of metal-oxide bilayers.

There was experimentally confirmed the possibility to decrease the degradation rate by doping of oxide film with nitrogen during metal oxidation [PALATNIK et al. 1982] or by doping of metal with nitrogen before its oxidation [KAMEI, MATSURAKI]. These approaches may be effective for making electronic devices with higher reliability and life time but their development requires the information about influence of impurity concentration and distribution of impurities in bilayers on the structure and properties of such devices. The dependence of relaxation processes in thermodynamically non-equilibrium multilayers on their chemical composition was the objective of this study.

2. Experimental details

The base metals investigated were prepared in the forms of foils and powders. Tantalum foils and powder contained impurities in quantities of (in ppm) Nb, <800; Fe, <70; Si, <80; W, <80; C, <100; 0, <300; N, <100. Niobium foils and powder contained impurities in quantities of (in ppm) Ta, <800; Fe, <70; Si, <70; Ti, <80; W, <80; C, <100; 0, <300; N, <100; H, <10. Tantalum and niobium foils were annealed during $t = 30$ min at temperature $T = 2100$ K in vacuum $P = 8 \cdot 10^{-4}$ Pa. Tantalum and niobium powders were sintered into porous tablets during $t = 30$ min at $T = 2100$ K and $P = 8 \cdot 10^{-4}$ Pa. Tantalum and niobium foils and powder tablets were doped by nitrogen during annealing at the $T = 1470-1520$ K in vacuum chamber filled by nitrogen up to pressure $P = 2 \cdot 10^{-1}$ Pa. Dielectric Ta_2O_5 and Nb_2O_5 films with thickness $h = 2 \cdot 10^{-7}$ m were grown on the surfaces of the base metals by the electrochemical oxidation in 0.01 M water solution of phosphoric acid to temperature. For electrical properties measuring of bilayers we used the semiconductor MnO_2 layer as an external electrode. Then the Me_2O_5 surfaces were convered by semiconductor MnO_2 layer using decomposition of liquid mangasnese nitrae in air for 5 min at $T = 500$ K according to the formula $Mn(NO_3)_2 \rightarrow MnO_2 + 2 NO_2+$ [BOIKO et al. 1995].

The chemical composition of foils was evaluated by Auger electron spectrometry (AES). The base pressure in the analysis chamber was $1 \cdot 10^{-7}$ Pa, energy of primary electrons was 3 keV. The depth of the analysed surface layer 5−10 Å. The Auger electrons were detected by a CMA (cylindrical mirror analyser) with an energy resolutionof 0.3%. To receive composition profiles the layers were etched by positive Ar ions with energy 3 keV. An estimation of the surface chemical composition of bilayers was made also by AES with amount of the relative sensitivity factors of the corresponding elements.

To intensify the degradation processes a heat treatment was applied to the studied layer systems. To stimulate the redox reaction at the Me/Me_2O_5 boundary all the annealed tantalum and niobium samples were heat treated at $T = 615$ K and $T = 525$ K correspondingly. This process causes a deficiency of oxygen in Me_2O_5 films.

As a result of redox reactions at the Me_2O_5/Me_2O_5 interface the oxidation of the nonstoichiometric Me_2O_5 takes place due to the extraction of oxygen from Me_2O_5 exhibiting the properties of a solid electrolyte.

These two redox reactions at the two interfaces (Me/Me_2O_5 and Me_2O_5/Me_2O_5) are interconnected with each other through conduction of oxygen ions in the dielelctric material. Thus, under heating, such trilayers ($Me-Me_2O_5-MnO_2$) display the properties of a galvanic cell [KROGER]. The temperatures 615 K and 525 K correspond to the conditions of the maximum output power generated by tantalum and niobium trilayers while
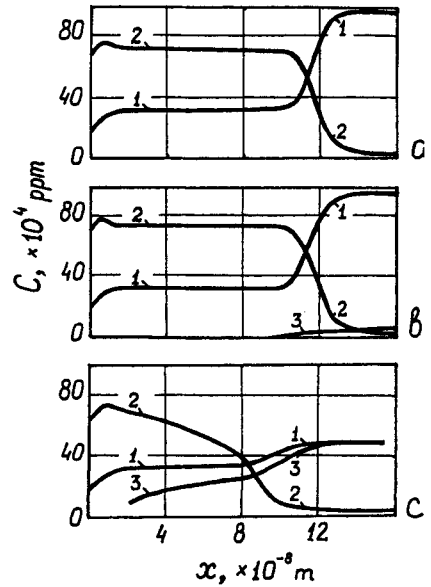
Fig. 1. Depth distribution of niobium (1), oxygen (2) and nitrogen (3) in bilayers prepared by anodic oxidation of pure niobium (a), solid solution of nitrogen in niobium (b) and niobium alloy with inclusions of niobium nitride (c)

functioning as galvanic by tantalum and niobium trilayers while functioning as galvanic cells. The properties of galvanic cells allow to determine the electrical parameters characterizing the following 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 a tangent of the plot's slope in the $\ln I_{sc}$-T^{-1} coordinates.

The conductivity of Me_2O_5 films 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

The chemical composition of the niobium-based bilayers and results of the electrical measurements after forming plane semiconductor contacts MnO_2 on the bilayer surfaces are presented in Fig. 1 and Table 1 correspondingly. They show that the anodic oxida-

Table 1

Values of electrical conductivity σ and dielectric constant ε of oxide films grown by anodic oxidation of pure niobium, solid solution of nitrogen in niobium and niobium alloy with inclusions of niobium nitride

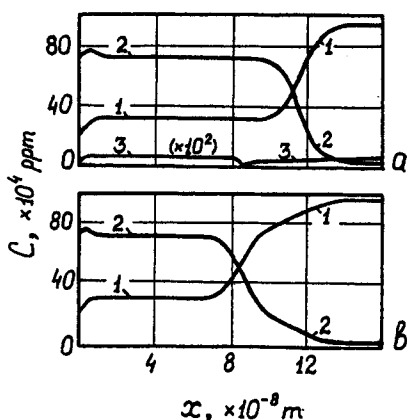| characteristics	Material for oxidation		
	pure niobium	solid solution of nitrogen in niobium	niobium alloy with niobium nitride
δ, Ohm^{-1} × m^{-1}	10^{-13}	10^{-13}	$2 \cdot 10^{-12}$
ε, arb. units	41	41	24

Fig. 2. Depth distribution of niobium (1), oxygen (2) and nitrogen (3) in bilayers prepared by anodic oxidation of solid solution of nitrogen in niobium (a) and pur niobium (b) after one-hour vacuum annealing

tion of pure niobium leads to growth of the stoichiometric oxid Nb_2O_5 (Fig. 1(a)) with minimum value of electrical conductivity σ and maximum value of dielectrical constant ε (Table 1). If the base metal contains the nitrogen the chemical composition , σ and ε of oxide strongly depend on nitrogen concentration in the niobium. So, if the nitrogen concentration doesn't exceed essent the nitrogen solubility limit in niobium at room temperature the AES don't register nitrogen in the Nb_2O_5 film which was formed by anodic oxidation of such, metal (Fig. 1(b)). In this case, according to

the Table 1 data, the values of σ and ε such film are close to corrrsponding ones of the Nb_2O_5 film formed on the pure niobium. ·In case of the oxinitride layer grown on the niobium alloy with nitride phase inclusions (Fig. 1(c)) the σ of such layer is higher and ε is lower as compared with pure Nb_2O_5 films (Table 1).

Distribution of chemical elements in bilayers on the base of both solid solutions of nitrogen in niobium and pure niobium after vacuum annealing of bilayers during 1 hour are shown in Fig. 2. One can see that the nitrogen concentration in oxide grown on the surface of solid solution of nitrogen in niobium is insignificant, near to sensibiliy limit of AES. At the same time the nitrogen concentration in the metal was $3 \cdot 10^4 - 4 \cdot 10^4$ ppm that exceeds its solubility limit in niobium at room temperature [FROMM, GEBHARDT]. Distribution of niobium and oxygen in bilayer on the base of metal doped by the nitrogen after annealing wasn't different from that in

bilayer on the base of undoped metal before annealing (Fig. 1(a)) and transition zone between metal and oxide was narrow. Distribution of chemical elements in bilayer on the base of undoped niobium after annealing (Fig. 2(b)) was different from initial state and width of the transition zone was increased. The conductivity of such bilayer was increased in comparison with nitrogen doped specimen.

The bilayers on the base of tantalum doped by nitrogen exhibited also better stability.

The $Me(Ta, Nb)-Me_2O_5-MnO_2$ trilayers on the base of both metals doped by nitrogen and pure metals were tested also in he regime of the galvanic cell for evaluation of their stability.

The dependences of $I_{sc}(T)$ for as-prepared $Me-Me_2O_5-MnO_2$ trilayer are shown in Fig. 3 where one can see that the value of I_{sc} higher for layer systems on the base of pure metals. Dissolution of nitrogen in metal is accompanied by growth of the activation
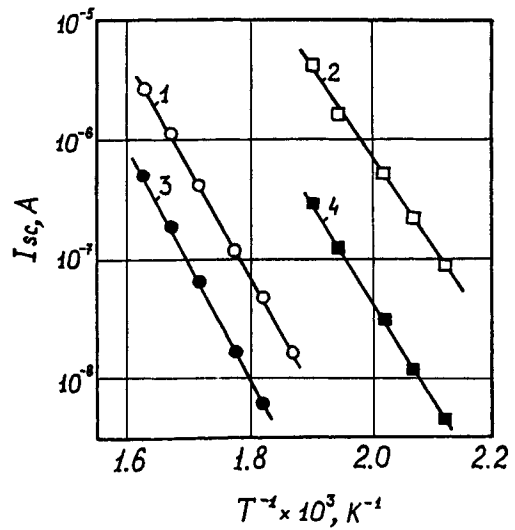
Fig. 3. The $I_{sc}(T)$ dependences for Ta–Ta$_{205}$–MnO$_2$ (1.3) and Nb–Nb$_{205}$–MnO$_2$ (2.4) trilayers made on base of the pure metals (1.2) and solid solution of nitrogen in the metals (3.4)

energy of oxygen ion transport W across the Ta–Ta$_{205}$–MnO$_2$ and Nb–Nb$_{205}$–MnO$_2$ layer systems from values 1.8 eV and 1.52 eV in the trilayers on the base pure metals to values 1.9 eV and 1.65 eV in the trilayers on the base of doped metals corresponding when the nitrogen concentration in the metals is near to the nitrogen solubility limit at room temperature. Therefore, the saturation is displayed in both the decrease of oxygen transfer rate across Me–Me$_{205}$–MnO$_2$ and the increase of the activation energy of this process. The barrier effect causes the stabilization of chemical composition and electrical properties of layer systems and, hence, increases the reliability and life time of electronic components based on such layer systems.

Usually, the materials used for electronic components contain different impurities. The most active interstitial impurity in tantalum and niobium is oxygen [FROMM]. The change of its concentration in metal can have inluence on the kinetics of oxygen trans-port across the layer system made on the base of such metal [PALATNIK et al.]. Presence of oxygen in metal hindered the dissolution of nitrogen. When oxygen concentration in niobium is more 10^4 ppm nitrogen isn't absorbed by metal (Fig. 4). Hence, preliminary
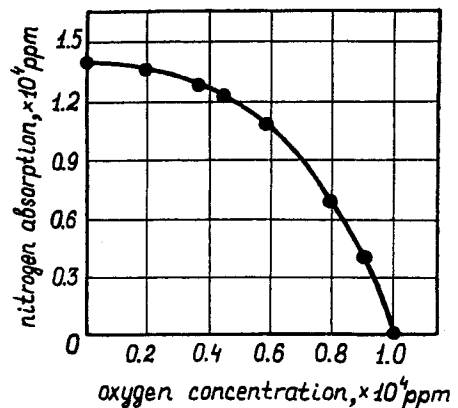
Fig. 4. The dependence of nitrogen absorption by niobium on oxygen concentration in the metal $(1.4 \cdot 10^4$ ppm-disso-lution limit of nitrogen in pure niobium at room tempera-ture)

refining of metal from oxygen is necessary to use nitrogen doping for improvement of metal-oxide bilayer stability.

Extraction of oxygen from treatment and niobium can be done by vacuum annealing at $T > 1970$ K [FROMM, GEBHARDT]. But this method can not be applied for sintered metally powders because the increase of sintering temperature leads to lossed of specific area of pores. Sometimes the process of such refining is very difficult, for example, when the oxygen concentration is near to its solubility limit in niobium at room temperature [POZDEEV-FREEMAN et al.].

The tantalum and niobium can be refined from oxygen with use of carbon or hydrogen [FROMM, GEBHARDT]. The application of carbon requires precise dose because carbon surpluses lead to formation of carbide phases which make difficult the growth of oxide film with homogeneous structure [FINCHAM, MARTIN]. Application of hydrogen is more perspective because its interaction with oxygen takes place at lower temperature $(T \sim 1000$ K [FROMM, GEBHARDT] as compared with carbon. Hydrogen surpluses can be extracted easily from metal during sintering of powder. Use of hydride niobium powders instead of pure niobium ones allows to decrease by factor of three or five the oxygen concentration in sintered powder and increase the effect of subsequent doping metal by nitrogen.

This study showed that the dissolution of nitrogen in Ta and Nb suppresses the degradation rate of Ta—$Ta_{2}O_{5}$ and Nb—$Nb_{2}O_{5}$ bilayers and increases reliability and life time of electronic devices made on their base. Preliminary purification of metals provides better positive effect of nitrogen doping on stability of structure and properties of metal-oxide bilayers. If the nitrogen concentration exceeds essentially the nitrogen solubility limit in metal at room temperature the dielectric properties of oxide on the metal surface are worse.

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