ISSN 1027-5495. Functional Materials, 26, No.2 (2019), p. 353-357.
doi:https://doi.org/10.15407/fm26.02.353 © 2019 — STC "Institute for Single Crystals"

Improvement of technology for the production of a semiconductor cathode of oxide-semiconductor capacitors

I.Sh.Nevludov, V.N.Gurin, D.V.Gurin, Yu.N.Oleksandrov, Ih.O.Yashkov

Kharkiv National University of Radio Electronics,
14 Science Ave., 61166 Kharkiv, Ukraine

Received November 8, 2019

Based on the Auger electron spectroscopy data on the chemical composition of the $Nb–Nb_2O_5–MnO_2$ system doped with indium oxide compounds, the ligature distributions across the thickness of MnO_2, Nb_2O_5 layers and also at the interface were determined. It was established that indium was present in both layers, but its maximum content was found at the MnO_2/Nb_2O_5 interface. To clarify the reasons for the decrease in leakage currents (I_{lc}) in the studied system doped with indium oxide, polarization studies of electrodes of pure niobium pentoxide and ones made from Nb_2O_5 containing indium inclusions were carried out. The results of the current-voltage measurements in the V(Y)–V(IY) oxidation-reduction system showed that in the presence of indium, the cathodic current decreases in proportion to the decrease in the leakage current. It was established that in the pyrolysis near the MnO_2/Nb_2O_5 interface in the absence of indium, a transition zone with a variable composition of manganese and niobium oxides appeared. Violation of the stoichiometric composition in MnO_2 and Nb_2O_5 layers adjacent to the interface was detected.
Keywords: manganese nitrate, manganese dioxide, auger spectroscopy, cathode coating quality.

На основе исследования методом электронной оже-спектроскопии химического состава системы $Nb–Nb_2O_5–MnO_2$ легированного оксидными соединениями индия, определено распределение лигатуры по толщине слоев MnO_2, Nb_2O_5, а также у поверхности раздела фаз. Установлено, что индий присутствует в обоих слоях, однако максимальное его содержание обнаружено на границе раздела фаз MnO_2/Nb_2O_5. Для выяснения причин снижения токов утечки (I_{ym}) в изучаемой системе, легированной оксидом индия проведены поляризационные исследования электродов из чистого пентаоксида ниобия и Nb_2O_5, содержащего включения индия. Результаты вольтамперных измерений в окислительно-восстановительной системе V(Y)–V(IY) показали, что в присутствии индия величина катодного тока снижается соизмеримо с уменьшением тока утечки. Обнаружено, что в отсутствие индия в процессе пиролиза вблизи границы MnO_2/Nb_2O_5 появляется переходная зона переменного состава оксидов марганца и ниобия. Установлено нарушение стехиометрического состава слоев MnO_2 и Nb_2O_5, прилегающих к поверхности.

Удосконалення технології отримання напівпровідникового катода оксидно-напівпровідникових конденсаторів. *І.Ш.Невлюдов, В.Н.Гурін, Д.В.Гурін, Ю.М.Олександров, І.О.Яшков.*

На основі дослідження методом електронної оже-спектроскопії хімічного складу $Nb–Nb_2O_5–MnO_2$ системи легованого оксидними сполуками індію, визначено розподіл лігатури за товщиною шарів MnO_2, Nb_2O_5, а також у поверхні розділу фаз. Встановлено, що індій присутній в обох шарах, однак максимальний його вміст виявлено на

кордоні розділу фаз MnO_2/Nb_2O_5. Для з'ясування причин зниження струмів витоку ($I_{св}$) у системі, що легована оксидом індію, проведено поляризаційні дослідження електродів з чистого пентаоксиду ніобію і Nb_2O_5, що містить включення індію. Результати вольтамперних вимірювань у окисно-відновнії системі V(Y)–V(IY) показали, що у присутності індію величина катодного струму знижується порівнянно зі зменшенням струму витоку. Виявлено, що під час відсутності індію у процесі піролізу поблизу кордону MnO_2/Nb_2O_5 з'являється перехідна зона змінного складу оксидів марганцю і ніобію. Встановлено порушення стехіометричного складу шарів MnO_2/Nb_2O_5, прилеглих до поверхні.

1. Introduction

Oxide-semiconductor capacitors (OSC) are widely used in the radio-electronic equipment due to an optimum combination of their electric parameters and dimensions and also due to an acceptable price policy [1, 2].

One of the problems in the production of OSC is the problem to provide a high-quality semiconductor layer ensuring the operational reliability of capacitors [3, 4]. Information about the chemical composition of such systems gives a possibility to establish a connection between their structures and electro-physical properties. Furthermore, it allows one to find ways of improving their technical production. One of such perspective methods is the modification of this system by doping its individual layers (Nb_2O_5 or MnO_2) with suitable oxide compounds. The known method to modify tantalum solid electrolytic capacitors consists in doping the semiconductor MnO_2 layer with oxides of rhodium, ruthenium, etc., which have a metallic conductivity [3–5].

It was shown that with these compounds it was possible to improve essentially the electro-physical properties of the MnO_2–Ta_2O_5 system, in particular, to decrease sharply the leakage current.

In the present paper, the doping of MnO_2 in the MnO_2–Nb_2O_5 system by injection of indium oxide with a high conductivity was carried out. The purpose of this work was to study the chemical composition and electrophysical properties of the MnO_2–Nb_2O_5 system after adding indium, as well as use the obtained results to improve the production technology of oxide-semiconductor capacitors.

2. Experimental

The experiments were carried out using the samples of the Nb–Nb_2O_5–MnO_2 system obtained by the following technique. A Nb_2O_5 layer was produced on a niobium foil with a thickness of 0.2 mm used as a substrate. The Nb_2O_5 layer was obtained by anodic oxidation of the foil for 3 h in a 5 % solution of orthophosphoric acid at the forming voltage U_f = 80 V. Then a polylayer film (16 layers) of MnO_2 or $MnO_2 + In_2O_3$ mixture was formed on the Nb_2O_5 surface by pyrolysis according to the following technology. The oxidized niobium samples were immersed in a water solution of manganese nitrate (or its mixture with indium nitrate) in the molar ratio of 140:1. After that, the nitrate film formed on the Nb_2O_5 surface was subjected to pyrolysis at a temperature of 240–270°C during 2–7 min for oxide formation. Then the next oxide layer was coated with the obtained film of MnO_2 (or its mixture with indium oxide) by the same technology. To get the necessary number of MnO_2 layers this process was repeated many times by employment of solutions with the subsequent concentration increase of $Mn(NO_3)_2$ or its mixture with $In(NO_3)_3$:25 % for the 1st and 2nd layers; 50 % for the 3d, 4th and 5th layers; 62 % for the remaining 11 layers. Since a partial destruction of Nb_2O_5 took place in the course of the pyrolysis, an intermediate anodic regeneration of niobium oxide was carried out after each formation of two layers of MnO_2. The anodic rege neration process was performed at the forming voltage U_f = 55 V.

The distribution of the elements in the layers of MnO_2 and Nb_2O_5 was studied by AES. To determine the composition of the MnO_2 semiconductor layer, these two layers were separated mechanically. On the other hand, when studying the dielectric Nb_2O_5 layer, the MnO_2 layer was preliminarily removed from this dielectric surface by boiling in a mixture of HNO_3 and HCl acids in the ratio of 3:1 during 1–2 h. The experiments were carried out by a commercial Auger spectrometer. The base pressure in the analysis chamber was $1{\cdot}10^{-10}$ Torr. Auger electrons were ejected by a primary electron beam with energy of 3000 eV. The information obtained under such conditions corresponds to a surface layer with a depth of 5–10 Å [6]. The Auger electrons were detected by a CMA (cylindrical mirror analyzer) with an energy resolution of 0.3 %. In the depth profile analysis, sputtering of the layers was done by a beam of positive Ar ions with energy of 3000 eV. An estimation

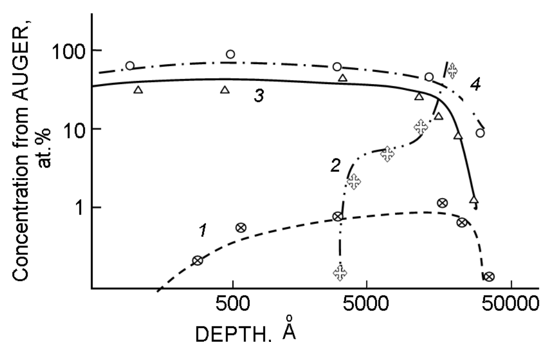


Fig. 1. Auger depth concentration profiles of the main components in the MnO_2 layer of the MnO_2–Nb_2O_5 system doped with indium (*1* — indium, *2* — niobium, *3* — manganese, *4* — oxygen).

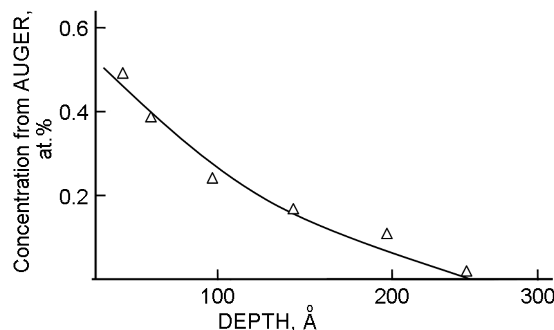


Fig. 2. Auger depth concentration profile of indium in the Nb_2O_5 upper layer of the MnO_2–Nb_2O_5 system doped with indium.

of the surface chemical composition was made by analyzing the intensity of the Auger peaks and the relative sensitivity factors of the corresponding elements [7]. The accuracy of the estimation was about 0.1 at % [8, 9].

The leakage current in the MnO_2–Nb_2O_5–Nb system, both in the presence of indium and without it, was measured with a commercial electrical bridge. The measurements were carried out in 10 % H_2SO_4 solution at the voltage of 55 V. In order to determine the influence of indium on the electrophysical properties of the Nb_2O_5 layer, a polarization study for pure Nb_2O_5 electrodes and for those doped by indium was performed. Voltage-current measurements were carried out in the potentiostatic mode with a potential sweep rate of 40 mV/s; an electrolyte of the following composition was used (mol/l): NH_4VO_3 — 0.195, $VOSO_4 \cdot 3H_2O$ — 0.195 and H_2SO_4 — 7.000. The potential values are given in relation to a normal hydrogen electrode.

3. Results and discussion

According to the results of the analysis of the EOS spectra, concentration profiles of the main components in the MnO_2–Nb_20_5 system doped with indium were constructed; these are presented in Figs. 1 and 2.

The concentration depth profiles of the distribution of the basic components in the MnO_2 and Nb_20_5 layers show that indium is present in both layers (Fig. 1, curve *1*). In the MnO_2 layer, the content of indium increases in the direction of the interface beginning from a depth of 250–300 Å from the MnO_2 external surface. The maximum content of indium is observed in the region adjoining the MnO_2/Nb_20_5 interface. In the Nb_20_5 layer the content of indium falls to zero at a depth of 300 Å (Fig. 2). Near the MnO_2/Nb_2O_5 interface there is a transition zone in which oxide compounds of manganese and niobium are present simultaneously (Fig. 1, curves *3* and *2*). The content of indium is practically constant in that zone.

An analysis of the ratios of manganese and indium to oxygen in the layers of 300 to 500 Å thick (Fig. 1, curves *2* and *3*) shows that the oxygen quantity is not enough for the formation of individual stoichiometric oxides of these elements. It allows for the assumption about formation of mixed manganese and indium oxides in this case. An investigation of the thermal decomposition of individual nitrates of these elements and their mixtures was carried out by a thermo-gravimetric method. It was shown that most of the endothermic effects in the derivatogram plotted for the salt mixtures were displaced towards a region of lower temperatures as compared with the individual salts. It is obvious that an intermediate substance of lower thermal stability forms in this case.

The results of X-ray phase analysis showed that the final products of the thermal decomposition of the individual manganese and indium nitrates in the temperature range of 240–300°C had a crystalline structure of MnO_2 or In_2O_3, whereas the products of pyrolysis of the nitrate mixture were X-ray amorphous substances. The obtained experimental results lead to the conclusion that during pyrolysis of the $Mn(NO_3)_2$ and $In(NO_3)_3$ mixture in the temperature range of 240–270°C the formation of mixed oxides of variable composition takes place in accordance with the thermochemical reaction:

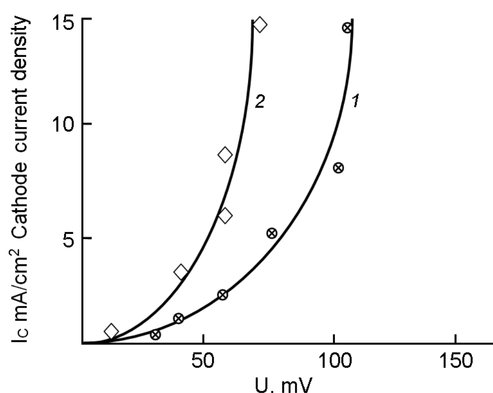
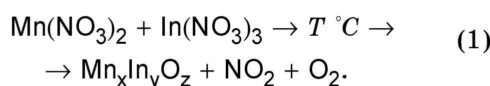


Fig. 3. Voltage-current characteristics of Nb_2O_5 electrode doped with indium (*1*) and without it (*2*).



$$Mn(NO_3)_2 + In(NO_3)_3 \rightarrow T\ ^{\circ}C \rightarrow \rightarrow Mn_xIn_yO_z + NO_2 + O_2. \quad (1)$$

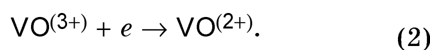
From the data shown in Fig. 1 one can see a specific distribution of indium in the MnO_2–Nb_2O_5 system with indium maximum concentration near the interface.

It is possible that such indium distribution is caused by technological peculiarities in the formation of this system. The low-stable mixed Mn and In oxides formed in the reaction (1) are probably partially decomposed during the polarization occurring in the periodic anodic re-generation of Nb_2O_5 layer, as it was described above. It may be supposed that released indium cations can migrate towards the MnO_2/Nb_2O_5 interface during the polarization. As a result, the accumulation of indium occurs in this region and its partial implantation into the surface layer of Nb_2O_5 takes place.

An investigation of the electro-physical properties of the MnO_2–Nb_2O_5–Nb system with the indium addition and without it showed that in the presence of indium the leakage current was five times lower.

Unfortunately, a complex indium distribution across the layer thickness in the investigated system (Fig. 2) makes it difficult to interpret the above experimental fact.

To clear up this question, an electrochemical study of an electrode produced from pure Nb_2O_5 and one doped with indium was carried out. The experiments were performed in the $V^{(4+)}$–$V^{(5+)}$ redox system where the reducing reaction occurs as a simple ion recharging by the scheme



$$VO^{(3+)} + e \rightarrow VO^{(2+)}. \quad (2)$$

Table 1. Range of $In(NO_3)_3 \cdot 4.5H_2O$ content in manganese nitrate solutions

No. s/n	Solution concentrations		
	$Mn(NO_3)_3 \cdot 6H_2O$		$In(NO_3)_3 \cdot 4.5H_2O$
	%	grams/liter	grams/liter
1	25	250	1–2,5
2	50	500	2–5,0
3	62	620	3–6

The results of voltage-current measurements are presented in Fig. 3. As one can see, the cathode current on the Nb_2O_5 electrode containing indium (curve *1*) is essentially lower than on the same electrode without addition of indium (curve *2*). For example, the cathode current is 4–5 times lower at the voltage of 65–80 mV. This value is in good accordance with the leakage current decrease which was found during the study of the electro-physical parameters of the Nb–Nb_2O_5–MnO_2 system doped with indium.

From the experimental data described above it could be concluded that the decrease of the leakage current in the investigated metal-oxide system is caused mainly by energy parameter changes of the Nb_2O_5 layer produced by injection of indium into the oxide structure.

4. Practical implementation of research results

As a result of the research, the optimal range of $In(NO_3)_3 \cdot 4.5H_2O$ content in manganese nitrate solutions was determined. The data obtained are shown in Table 1.

The optimal values of the content of $In(NO_3)_3 \cdot 4.5H_2O$ in manganese nitrate solutions are included in the current process at the stage of manufacturing the oxide-semiconductor capacitors. The basis for this was the data obtained on the testing products with nominal parameters: 16 V×68 μF, 20 V×47 μF. The results of measurements of the OSC electro-physical parameters are given in Table 2.

The introduction of the indium additive as $In(NO_3)_3 \cdot 4.5H_2O$ into the $Mn(NO_3)_3 \cdot 6H_2O$ solution does not significantly increase the complexity of the technological process, while this considerably pays off by improving the OSC electro-physical parameters.

Table 2. Electro-physical parameters of OSCs

No. s/n	Semiconductor layer	C, μF	tgδ	I_{lc}, mA
1	With additive	16.05	2.8	2.5
2	With additive	4.1	1.74	1.45
3	No additive	16.2	12.5	15.4
4	No additive	4.4	8.0	4.0

4. Conclusions

The obtained data show that during the formation of a MnO_2 semiconductor layer on a Nb_2O_5 substrate in the presence of indium, the implantation of indium into the Nb_2O_5 dielectric surface layer takes place. This results in a change of the electro-physical characteristics of the MnO_2–Nb_2O_5 system, in particular in a decrease of the leakage current. During pyrolysis, the thermo-diffusion of niobium into the MnO_2 layer occurs, and a transition zone containing mixed oxides of manganese and niobium forms. A thin semiconductor interlayer adjacent to the MnO_2/Nb_2O_5 interface becomes enriched with niobium. Simultaneously, there is a violation of the stoichiometric composition of the dielectric surface due to niobium deficiency.

The effect of indium-containing additives on the electro-physical parameters of the OSC when introducing the additives into the manganese nitrate solution has been investigated. The implementation of the results into the existing technology has provided oxide-semiconductor capacitors with improved parameters.

A further task of the authors is to develop the procedure of indium recovery from $Mn(NO_3)_3{\cdot}6H_2O$ + $In(NO_3)_3{\cdot}4.5H_2O$ nitrate solutions due to the ability of $In(OH)_3$ to dissolve in an excess of alkali to form complex hydro oxidants.

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