ISSN 2522-9818 (print)
Сучасний стан наукових досліджень та технологій в промисловості. 2018. № 4 (6) ISSN 2524-2296 (online)

UDC 537.33.3 DOI: https://doi.org/10.30837/2522-9818.2018.6.057

I. NEVLUDOV, V. GURIN, D. GURIN

METHODS OF FAILURE DIAGNOSTICS OF TANTALUM OXIDE-SEMICONDUCTOR CAPACITORS WITH SOLID DIELECTRIC

The subject of the study is oxide-semiconductor capacitors, which are widely used in the manufacture of electronic equipment. **The goal of the study** is to determine the main causes of failures of oxide-semiconductor capacitors at the production and operation stages. For this purpose, analogs of flat film capacitors have been built, which represented various production and operational situations (including dielectric breakdown); the structures of individual layers of capacitors, their chemical and phase formulas and electrical properties were found. Since capacitor anodes have a porous structure and are not subjected to the usual methods of studying flat objects, we used the simulation method. The simulated data were compared with the corresponding values measured on capacitors that did not work during operation or testing. **In the process of research**, the following tasks were solved: physical phenomena occurring in capacitors under the influence of various factors appearing in the production process were considered. It is shown that redox processes lead to deterioration of the capacitors. It is established that the main causes of the degradation of capacitors are thermodynamic in nature and they reduce the lifetime of the capacitors. Technological operations have been developed that significantly reduce or eliminate the types of failures considered. These include the basic operations of the process. Doping of the anodes of the capacitors with nitrogen. This operation is performed simultaneously with the sintering of porous anodes and contributes to the increase of the lifetime, operating temperatures and reverse voltage of the capacitors. Growing a multilayer dielectric by cyclically changing the formula of the electrolyte, where anodizing occurs. Formation of a dense cathode by applying an alternative electric field when impregnating porous anodes. Organic silicon impregnation of capacitors' sections. This creates a dense waterproof film that blocks areas of free dielectric contact with manganese dioxide and provides good adhesion of the protective organic film to the section. The following **methods** were used in the work: electron beam probing, Auger spectroscopy and microprobe measurements.

Keywords: oxide-semiconductor capacitor; simulation method; failure analysis.

Introduction

Oxide-semiconductor capacitors find broad application in the radio-electronic equipment thanks to an optimum combination of their electric parameters to overall dimensions and also thanks to acceptable price policy [1–4].

Analysis of problems and statement of tasks

In the course of production and operation parametrical failures of capacitors often take place that does relevant development of a technique of the analysis of failures of capacitors at a production stage. Such technique will allow producers to increase quality of the products and will reduce number of claims from the enterprises which use oxide-semiconductor capacitors. The purpose of the real work is development of a technique of identification of potentially unreliable capacitors, on the basis of studying of features of the processes resembling in them

As capacitor anodes are of porous structure and not subject to conventional methods of investigation of planar objects we have employed the simulation technique.

Flat film capacitor analogs were constructed that represented various production and operation situations (including dielectric breakdown); then by means of electronic beam, Auger-spectroscopy and microprobe measurements we found out the structures of separate capacitor layers, their chemical and phase formulae and electric properties.

Results of the specified researches are published in [5–11].

The simulated data were compared to the corresponding values measured on the capacitors that failed while operating or being tested. As our industry produces, together with tantalum capacitors, niobium ones that fail more often, the total number of capacitors investigated within 10 years amounts to several hundred.

The diagnostics techniques proposed comprise the following.

Presenting main material

1. Analyzing failure causes.

The analysis (which is of non-destructive nature) is made on the grounds of the results of studying the influence of external direct voltage value and polarity, alternate voltage component frequency, temperature and environmental conditions on main electric properties of the capacitors. The analysis makes it possible to locate the defect that caused the failure and to detect the production procedure responsible for this defect. To revise the results of the analysis they sometimes practice layer etching and visual examination of capacitors' components.

The figure 1 shows the characteristic dependencies of leakage current (I) on voltage (U), temperature (T) and duration (t) of vacuum drying of unsealed capacitors that correspond to various failure causes.

A. Normal capacitor

(a) dependency I(U) is an asymmetric one (1) with U>0 I ~ exp U, U < O I~U, where 2 < n < 3;

(b) dependency I(T) is an activation one (1) with activation energy E > 0.5 eV;

(c) I(t) = const, i.e. drying does not influence the current.

B. Metal shunt

Appears because of solder streaking during capacitor sealing or because of forming metal threads while welding tantalum and nickel leads.

(a) dependency I(U) is a symmetric and linear one (2): I = <S U;

(b) dependency I(T) is a non-activation one (2): the current decreases reversibly with T growth;

(c) I (t) = const (2).

They are the procedures of nickel lead welding and casing insulator soldering that are responsible for the failure dependency I(T) is a non-activation one (3): the current decreases irreversibly with T growth.

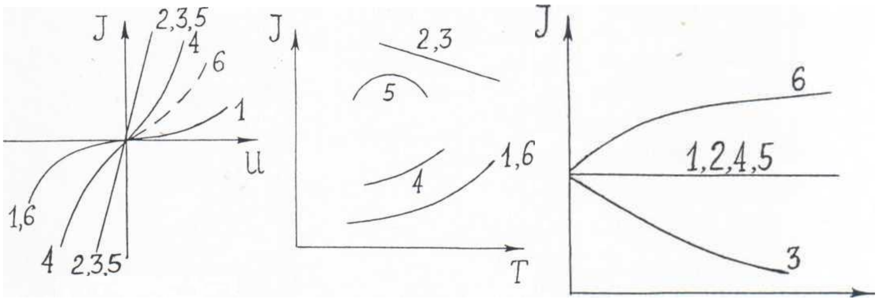

Fig. 1. The characteristic dependencies of leakage current (I) on voltage (U), temperature (T) and duration (t) of vacuum drying of unsealed capacitors that correspond to various failure causes

C. Non- metal shunt

It appears because of penetration of the moisture to the internal insulator or capacitors anode lead surface.

(a) dependency I(U) is a symmetric ad linear one (3): I - G U;

(b) dependency I(T) is a non-activation one (3): the current decreases irreversibly with T growth;

(c) while drying the current decreases irreversibly.

They are section drying procedure preceding to sealing and insulator cracks that are responsible for the failure.

D. Dielectric breakdown with limitation of input power

It occurs in presence of latent flaws in the dielectric and close dielectric-semiconductor cathode contact in the flawed spot. Power limitation is related to the local reduction of the cathode to the lower manganese oxides with high resistance.

(a) dependency I(U) is a symmetric one (4) with I ~ Un, where 1.5 < n < 2.5

(b) dependency I(T) is an activation one (4) with activation energy E ~ 0.1 eV;

(c) I (t) = const (4).

It is anode sintering as well as powder quality that are responsible for the failure.

E. Catastrophic breakdown

It occurs in presence of latent flaws on the internal surface of the dielectric and in absence of close dielectric-cathode contact in the flawed spot and also on penetration of carbon layer through manganese dioxide to the dielectric surface.

(a) dependency I(U) is a symmetric and linear one (5) with I = G7 U;

(b) dependency I(U) is not monotonous (5) for the thermal coefficient of resistance changes its sign;

(c) I (t) = const (5).

They are anode sintering and pyrolytic manganese dioxide deposition procedures that are responsible for the failure.

F. Parametric failure

It occurs in presence of flaws due to reduction of the dielectric by the anode and in absence of dielectric-cathode close contact in the flawed spots.

(a) dependency I(U) is an asymmetric one (6) with U<0 I ~ Un, where 2<n<3;

(b) dependency I(T) is an activation one (6) with activation energy E = 0.5 eV;

(c) while drying the current increases reversibly (6) and on moistening it decreases.

It is manganese dioxide pyrolytic deposition procedure that is responsible for the failure.

2. Main production procedures control.

Some failure analysis techniques can also be made use of as simple, express and information-yielding techniques of controlling the following procedures: sintering of anodes, growing oxide dielectric and semiconductor cathode deposition. Conventional control techniques for these procedures based upon measuring capacitors' performance characteristics are rough and don't give evidence of latent flaws that can cause spoilage on the final production stage or an operation failure. The control techniques proposed allow to detect such flaws in the early production stages and to correspondingly modify the production procedures or materials used.

3. Shot-time lifetime estimation.

As a result of the investigation made it was found out that the main causes of degradation of capacitors are of thermodynamic nature, they reduce capacitors' lifetime and are as follows: a) local dielectric film reduction by the b) field crystallization and splitting of anode amorphous dielectric (fig. 2).

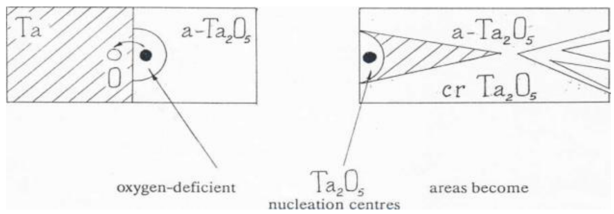

Fig. 2. Illustration of the main causes of capacitor degradation

ISSN 2522-9818 (print)
Сучасний стан наукових досліджень та технологій в промисловості. 2018. № 4 (6) ISSN 2524-2296 (online)

The same redox processes as those causing deterioration of capacitors cause them functioning in current-generator mode (fig. 3).

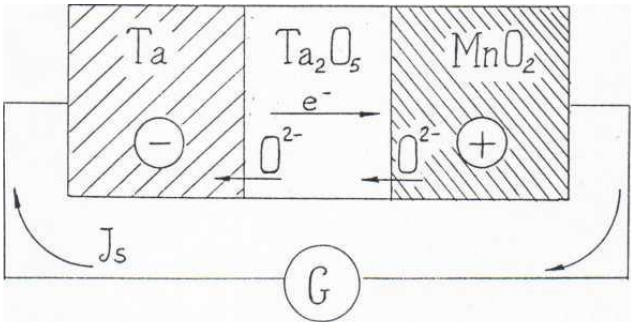

Fig. 3. Capacitor operation in current generator mode

The temperature being high, the disconnected electrodes of a capacitor generate an EMF; on connection of the electrodes the galvanometer register a short-circuit current Is.

A short-time investigation of temperature and temporal relations between the EMF and Is allows to determine all necessary values and to estimate the capacitor's lifetime according to the formula

$$\tau = \tau_0 \left(\frac{E - aU}{KT} \right).$$

There exists a strict correspondence between E values taken from test results and those derived from the Is(T) dependence that proves the validity of the technique proposed. The said technique allows to promptly estimate the lifetime of serial capacitors and the ones produced under new techniques or of new materials.

A good correspondence was obtained for serial capacitors between the real pre-failure operating time and the lifetime estimated with the help of the technique proposed.

4. Method of sorting unreliable capacitors out.

These methods can be used either by the manufacturer or by the customer while checking manufactured or purchased capacitors.

The mentioned methods are based on the two physical phenomena:

- pulse electric strength of a dielectric is correlated to its lifetime under the normal conditions;
- dielectric conductivity asymmetry is sensitive to the primary stages of flaw generation in the dielectric.

On these grounds simple, reliable and express methods of sorting out unreliable capacitors were developed comprising breakdown simulator and current comparator under different external voltage polarity signs; they allow rejecting - on the voltage pulse at the check-out element - latently flawed capacitors without damaging the rest of them.

Joint 1000-hour tests with a set of rejected capacitors and a random sample of capacitors that successfully passed through the sorting (initially all the capacitors had the same current leakage level) resulted as follows: failure was registered with 70 per cent of the rejected capacitors the rest of them having elevated current leakage values while the comparison sample did not give neither failures nor changes in current leakage.

Technological operations provide significant reduction or eliminate the considered types of failures.

1. This procedure is executed simultaneously with the sintering of porous anodes and allows to:

a) create in the anode a diffusion barrier for oxygen at the oxide dielectric interface raise electrons' energy barrier and electron gap concentration in the dielectric;

b) owing to that dielectric reduction and anode-dielectric electron injection are suppressed which process contributes to raising the lifetime, operating temperatures and reverse voltage of capacitors.

2. Growing a multi-layer dielectric.

To grow a multi-layer dielectric, one should change in a cyclic manner the formula of the electrolyte where anodization is taking place.

Thus, treated the dielectric forms layers with the dimensions considerably less than those of the amorphous dielectric critical nucleation center (Rcr = 100nm).

Owing to that dielectric crystallization is suppressed that contributes to raising the lifetime and operation temperature of capacitors.

3. Dense cathode deposition.

Owing to the alternate electric field application while impregnating porous anodes with manganese nitrate flawed spots within the dielectric become manganese dioxide deposition centers.

This technique provides for blocking the flaws and for a close contact between the cathode and the dielectric for manganese dioxide islets on the surface of the dielectric become the centers of the ensuing deposition of pyrolytic manganese dioxide.

Another way to improve the quality of the cathode layer can be doping manganese nitrate with a doping solution containing indium [12–15].

It was found that when a semiconductor MnO_2 layer forms on the Nb_2O_5 substrate in the presence of indium, indium is implanted into the Nb_2O_5 surface layer of the dielectric, which leads to a change in the electrical characteristics of the $MnO_2 - Nb_2O_5$ system, in particular, to a decrease in leakage current. During pyrolysis, thermal diffusion of niobium into the MnO_2 layer occurs, as well as a transition zone containing mixed oxides of manganese and niobium. A thin semiconductor layer adjacent to the MnO_2 / Nb_2O_5 interface is enriched with niobium. At the same time, the stoichiometric composition of the dielectric surface associated with the niobium deficiency changes.

The introduction of indium containing additives into a solution of manganese nitrate causes a decrease in the pyrolysis temperature, which prevents the appearance of defects in the dielectric film by the action of temperature.

ISSN 2522-9818 (print)
ISSN 2524-2296 (online) Innovative technologies and scientific solutions for industries. 2018. No. 4 (6)

4. Organic silicon impregnation of capacitors' sections.

As a result of organic silicon impregnation of capacitors' sections and ensuing impregnate polymerization a dense water-proof film is generated that blocks the areas of loose manganese dioxide-dielectric contact and provides for a good adhesion of the protective organic film to the section.

This technique prevents moisture from affecting the free surface of the dielectric film. Owing to that the lifetime and reliability of capacitors increase.

Thus, increase the lifetime and reliability of capacitor.

Conclusions

Simple, reliable, and rapid methods for sorting unreliable capacitors have been developed, including a breakdown simulator and a current comparator with different external signs of voltage polarity; they allow deflecting - on the voltage pulse on the switching off element - latently defective capacitors without damaging the rest.

All the diagnostics and inspection methods proposed had been developed under serial production conditions and turned out to be efficient enough. Technological operations are developed that significantly reduce or eliminate the considered types of failures.

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Received 31.10.2018

Відомості про авторів / Сведения об авторах / About the Authors

Невлюдов Ігор Шакирович – доктор технічних наук, професор, Харківський національний університет радіоелектроніки, завідувач кафедри комп'ютерно-інтегрованих технологій, автоматизації та мехатроніки, Харків, Україна; e-mail: igor.nevliudov@nure.ua; ORCID ID: https://orcid.org/0000-0002-9837-2309.

Невлюдов Игорь Шакирович – доктор технических наук, профессор, Харьковский национальный университет радиоэлектроники, заведующий кафедрой компьютерно-интегрированных технологий, автоматизации и мехатроники, Харьков, Украина.

Nevliudov Igor – Doctor of Sciences (Engineering), Professor, Kharkiv National University of Radio Electronics, Head at the Department of Computer-Integrated Technologies, Automation and Mechatronics, Kharkiv, Ukraine.

Гурин Валерій Миколайович – доктор технічних наук, професор, Харківський національний університет радіоелектроніки, професор кафедри економічної кібернетики та управління економічною безпекою, Харків, Україна; e-mail: valerii.hurin@nure.ua; ORCID ID: https://orcid.org/0000-0001-7536-2186.

Гурин Валерий Николаевич – доктор технических наук, профессор, Харьковский национальный университет радиоэлектроники, профессор кафедры экономической кибернетики и управления экономической безопасностью, Харьков, Украина.

Gurin Valeriy – Doctor of Sciences (Engineering), Professor, Kharkiv National University of Radio Electronics, Professor at the Department of Economic Cybernetics and Economic Security Management, Kharkov, Ukraine.

Гурін Дмитро Валерійович – Харківський національний університет радіоелектроніки, аспірант кафедри комп'ютерно-інтегрованих технологій, автоматизації та мехатроніки, Харків, Україна; e-mail: dmytro.gurin@nure.ua; ORCID ID: https://orcid.org/0000-0002-2272-5227.

Гурин Дмитрий Валерьевич – Харьковский национальный университет радиоэлектроники, аспирант кафедры компьютерно-интегрированных технологий, автоматизации и мехатроники, Харьков, Украина.

Gurin Dmytro – Kharkiv National University of Radio Electronics, Postgraduate Student at the Department of Computer-Integrated Technologies, Automation and Mechatronics**,** Kharkiv, Ukraine.

МЕТОДИ ДІАГНОСТИКИ ВІДМОВ ТАНТАЛОВИХ ОКСИДНО-НАПІВПРОВІДНИКОВИХ КОНДЕНСАТОРІВ З ТВЕРДИМ ДІЕЛЕКТРИКОМ

Предметом дослідження є оксидно-напівпровідникові конденсатори, які широко застосовуються у виробництві радіоелектронної апаратури. **Метою** дослідження є з'ясування основних причин відмов оксидно-напівпровідникових конденсаторів на стадії виробництва і в експлуатації. З цією метою побудовані аналоги плоских плівкових конденсаторів, які представляли різні виробничі і експлуатаційні ситуації (включаючи діелектричний пробій); були виявлені структури окремих шарів конденсаторів, їх хімічні та фазові формули і електричні властивості. Оскільки конденсаторні аноди мають пористу структуру і не піддаються звичайним методам дослідження плоских об'єктів, ми використовували метод моделювання. Моделюються дані порівнювалися з відповідними значеннями, виміряними на конденсаторах, які не спрацьовували при роботі або тестуванні. У процесі дослідження вирішено такі **завдання**: розглянуті фізичні явища, що відбуваються в конденсаторах при впливі різних факторів, що з'являються в процесі виробництва. Показано, що окислювально-відновні процеси призводять до погіршення стану конденсаторів. Встановлено, що основні причини деградації конденсаторів мають термодинамічний характер і вони зменшують час життя конденсаторів. Розроблено технологічні операції, які значно зменшують або виключають розглянуті види відмов. До них відносяться основні операції технологічного процесу. Легування анодів конденсаторів азотом. Ця операція виконується одночасно зі спіканням пористих анодів і сприяє підвищенню часу життя, робочих температур і зворотної напруги конденсаторів. Вирощування багатошарового діелектрика шляхом циклічної зміни формули електроліту, де відбувається анодування. Формування щільного катода шляхом застосування альтернативного електричного поля при просочуванні пористих анодів. Просочування органічним кремнієм секцій конденсаторів. При цьому створюється щільна водонепроникна плівка, яка блокує ділянки вільного діелектричного контакту з діоксидом марганцю і забезпечує хороше зчеплення захисної органічної плівки з секцією. У роботі використані **методи**: зондування електронним пучком, оже-спектроскопія і мікрозондового вимірювання.

Ключові слова: оксидно-напівпровідниковий конденсатор; метод моделювання; аналіз відмов**.**

МЕТОДЫ ДИАГНОСТИКИ ОТКАЗОВ ТАНТАЛОВЫХ ОКСИДНО-ПОЛУПРОВОДНИКОВЫХ КОНДЕНСАТОРОВ С ТВЕРДЫМ ДИЭЛЕКТРИКОМ

Предметом исследования являются оксидно-полупроводниковые конденсаторы, которые широко применяются в производстве радиоэлектронной аппаратуры. **Целью** исследования является выяснение основных причин отказов оксидно-полупроводниковых конденсаторов на стадии производства и в эксплуатации. С этой целью построены аналоги плоских пленочных конденсаторов, которые представляли различные производственные и эксплуатационные ситуации (включая диэлектрический пробой), были обнаружены структуры отдельных слоев конденсаторов, их химические и фазовые формулы и электрические свойства. Поскольку конденсаторные аноды имеют пористую структуру и не поддаются обычным методам исследования для плоских объектов, мы использовали метод моделирования. Моделируемые данные сравнивались с соответствующими значениями, измеренными на конденсаторах, которые не срабатывали при работе или тестировании. В процессе исследования решены следующие **задачи**: рассмотрены физические явления, происходящие в конденсаторах при воздействии различных факторов, появляющихся в процессе производства. Показано, что окислительно-восстановительные процессы приводят к ухудшению состояния конденсаторов. Установлено, что основные причины деградации конденсаторов имеют термодинамический характер и они уменьшают время жизни конденсаторов. Разработаны технологические операции, которые значительно уменьшают или исключают рассмотренные виды отказов. К ним относятся основные операции технологического процесса. Легирование анодов конденсаторов азотом. Эта операция выполняется одновременно со спеканием пористых анодов и способствует повышению времени жизни, рабочих температур и обратного напряжения конденсаторов. Выращивание многослойного диэлектрика путем циклического изменения формулы электролита, где происходит анодирование. Формирование плотного катода путем применения альтернативного электрического поля при пропитке пористых анодов. Пропитка органическим кремнием секций конденсаторов. При этом создается плотная водонепроницаемая пленка, которая блокирует участки свободного диэлектрического контакта с диоксидом марганца и обеспечивает хорошее сцепление защитной органической пленки с секцией. В работе использованы **методы**: зондирование электронным пучком, оже-спектроскопия и микрозондового измерения.

Ключевые слова: оксидно-полупроводниковый конденсатор; метод моделирования; анализ отказов.