Ti - Vacuum Deposition onto Al Substrate to Produce Cathode Foil for Oxide Electrolytic Capacitors

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Introduction

The critical factors of modern capacitors are: (i) their sizes and weight which have to be constantly reduced to meet fast-growing demand of the electronics and (ii) the equivalent series resistance (ESR) calling for decreasing power dissipation in capacitors.
The cathode foil (CF) being as basic component of a capacitor both oxide-electrolytic and with conducting polymer electrolyte makes its own contribution into its miniaturization. It occurs, first of all, as a result of CF specific capacitance (SC) and, consequently capacitor SC. Besides, a lower CF thickness does also help in capacitor miniaturizing.
At present CF is made by using a conventional unsafe method for electrochemical etching (ECE) of aluminium (Al) foil surface to develop its area. The ECE - process is not only the most expensive technological component in the capacitor production chain; its abilities to increase the foil surface area are practically exhausted and therefore the SC of such CF can not be higher than 500 – 600 $\mu F/cm^2$. These figures for CF is far behind of the modern anode foil requirements when the CF must possess SC more than 1500 – 2000 $\mu F/cm^2$ so as to fully use the anode capacitance in the advanced low voltage technique [1-3].

High capacitance CF being produced by PVD - method

In order to meet the modern anode foil the OKB TITAN Ltd, a Russian R & D company dealing with cathode and anode foils for capacitors, has worked out and put into life a new industrial coil technology to produce high capacitance CF with SC of 2000 – 3000 $\mu F/cm^2$ by using a vacuum electron beam (EB) technology for coating deposition onto Al-foil representing the family of PVD – method [4-6].
The general view photo of the installation to manufacture CF with a coating being deposited by the EB - technology is presented in Fig.1 and the basic sketch for the technology is given in Fig.2. Looking at Fig.2 one can see that the coating onto aluminium (Al) foil is formed by EB evaporation of titanium (Ti) from a water-cooled crucible followed by material condensing out of a vapor phase in nitrogen (N) atmosphere, while the Al-foil constantly moving over the evaporator. The CF with a highly developed surface area is made by EB – technology to deposit a highly porous films of Ti its nitrides and oxides of 0,3 ÷ 0,8 μm in thickness on each Al-foil side.

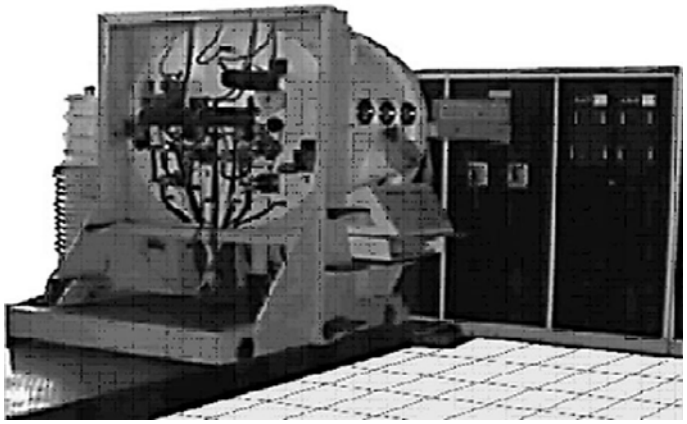
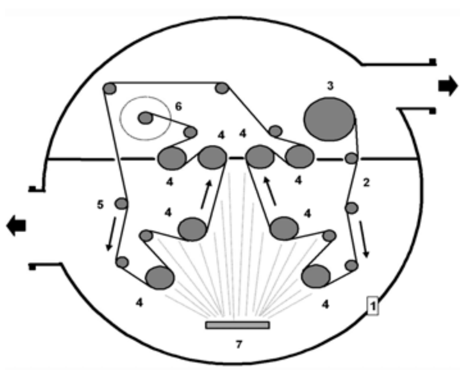


Fig. 1. The general view of EB – installation to coat Al-foil



1 – Vacuum chamber
2 – Al foil
3 – Recoiling roll
4 – Cooled roll
5 - Roll
6 –Coiling roll
7 - Evaporator

Fig. 2. The Sketch for Electron Beam (EB) – technology to coat both Al -coil sides

The EB - technology developed by the OKB TITAN making it possible to produce high capacitance CF is an ecologically safe kind for it does not both utilize harmful for a human-being substances and pollute environment that drastically reduces production expenses.

It is to be only noted that Ti is one of the most suitable metals to be employed for deposit porous coatings onto Al - foil. Ti is well evaporated, possesses excellent adhesiveness due to its high condensate energy, corrosion and heat proof, compatible to Al, mechanically strong and light, non-magnetic that is important for radio electronics and electro technique. Ti easy forms nitrides which have higher electro conductivity that makes such a CF very attractive for capacitors with conducting polymer electrolyte.

<u>The properties of the CF with the coating deposited by the EB - technology</u>

The basic characteristics for the CF of the EB – treatment and the CF being produced by electrochemical method to develop its surface area is given in Table 1.

Table 1

Parameters name and measurement units	Technologies employed and Company Name		
	Electrochemical etching		PVD – method (EB – Technology)
	Elekond, Russia	JCC, Japan	OKB TITAN, Russia
Al - foil thickness, μm	50	50	20 ÷ 40
Specific capacitance (SC), μF/cm^2	200	500	600÷3000
Capacitance storage losses, %	n.a.	minus 10	minus 10
Capacitance boiling deviation, %	minus 10	+ 4	+ 5
Chlorine ions content, mg/m²	0,5	0,3	0,1
Capacitor equivalent series resistance (ESR), milliohm	n.a.	7	5

As known, generally, the key criteria to evaluate the CF are SC (which is defined by effective surface area and electro physical characteristics of the coating sputtered), the SC time stability (which depends upon the corrosion resistance of the coating deposited inside electrolytes) and the physic-mechanical properties of the coating and its adhesion to substrate.

The Table 1 shows that the basic quality parameters of the CF coated by EB – technology (EB-CF) are much better than the same of the CF with ECE – surface (ECE-CF).

It is to be noted the EB – technology allows to produce considerably thinner CF (20-40 μm against 50 μm after ECE – treatment) that promotes capacitors miniaturization.

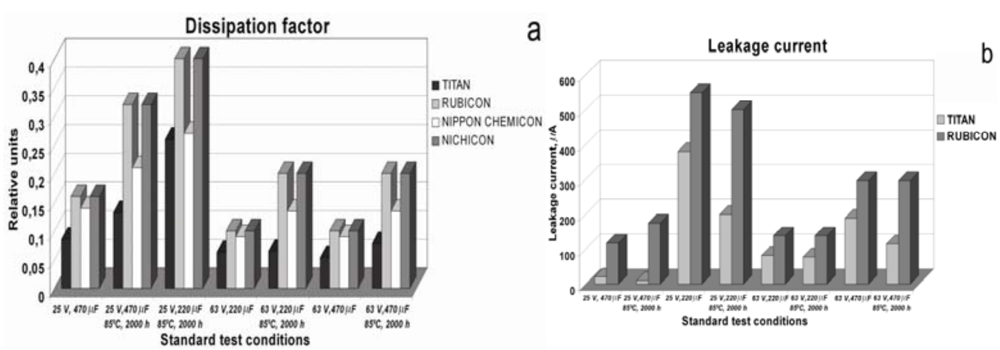


Fig. 3 a & b. Comparison data of Load Life Test (test temperature 85^o C and duration 2000 hours; voltage: 25 and 63 V; capacitance: 220 and 470 μF) for the experimental capacitors with EB-CF as cathode and the standard characteristics for conventional capacitors with cathode of ECE–CF.: (a) Dissipation factor and (b) Leakage current.

That difference in CF parameters has been also confirmed while comparing the results of the Load Life Test for the experimental capacitors where EB-CF was employed as cathode and the standard characteristics for conventional capacitors with cathode of

ECE– CF. The comparison data are given in the Fig 3,a & b. It says that the both parameters - dissipation factor (Fig.3 a) and leakage current (Fig. 3 b)-, are much better for EB-CF.

Chemical composition and microstructure of EB - coating

The above comparison data on the study of: (i) the basic parameters for EB-CF and ECE-CF and (ii) leakage current and dissipation factor for EB-CF experimental capacitors and the standard characteristics for conventional ECE-CF capacitors has been supplemented with the investigations of chemical composition and microstructure of the coatings to be deposited under the OKB TITAN EB – technology with a view of understanding the physical nature of EB-CF high properties.

(i) To study the coating chemical content was utilized X-ray Photoelectron Spectrometer (XPS). The XPS - Spectrograms are shown in the Fig. 4. According to the data the basic coating components are Ti, TiO_x -TiN, TiO_2. In the depth of 250 angstroms the percentage relationship between Ti:O:N was 38:33:29. It speaks of the high content for Ti – oxides that is connected, above all, with the presence of considerable amount of the atomic oxygen in the working chamber. It is to be kept in mind that the oxides worsen the resistance parameter. The latter, obviously, is one of the factors which extend the diapason of SC for EB-CF. Nevertheless, the figures of the basic parameters for EB-CF remain better than for the ECE-CF

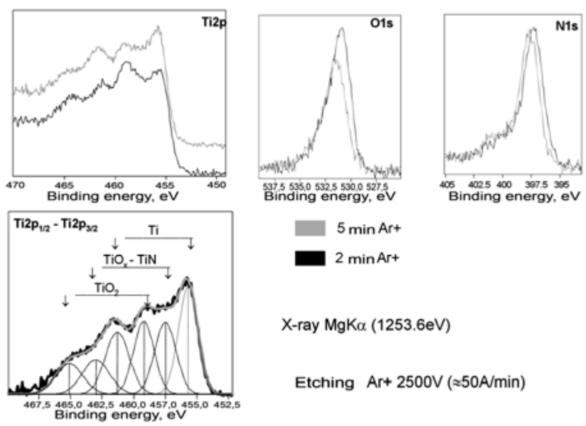
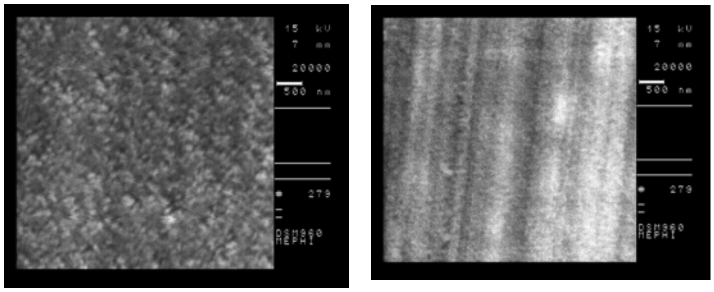


Fig. 4. XPS – spectrograms of the CF - coating being sputtered by EB-technology

(ii) The microstructure of the EB-CF coatings having been investigated with the Electronic Microscope –DSM960 is shown in the Fig. 5,a & b. The results witness of non-homogeneous microstructure in the coating itself: there are both practically ideal areas of nanosized crystals (Fig. 5,a) and enclaves of mixed microstructure (Fig. 5,b).



(a) nanosized structure (b) mixed microstructure

Fig 5,a & b. Microstructure of CF- coating being deposited by EB - technology (x20000)

According to the modern nanostructure material science one of the basic methods to produce nanomaterials is a film technology which also includes the physical deposition from gaseous phase (PVD - method). For example, sputtering TiN-films of 1 μm in thickness the grain size is 5-30 nm [7]. The appearance of nanosized crystals which naturally leads to forming multi surfaced borders in the nanomaterials is the base for substantial change of solid body properties as a result of both structure modification & electrons and new possibilities to add various alloys of different chemical nature & atomic sizes. Besides, as known, in a nanosized diapason the quant-mechanical substance properties start appearing that brings about changing basic material characteristics. It means that the creation of nanocrystal structures is of great importance to manufacture structural and functional materials and coatings.
The above said permits to note that the coating microstructure with nanosized grains leads to forming numerous division planes. The latter tremendously increases not only the surface area development of CF but also considerably improves CF SC and ESR of capacitors (please, see Table 1).
The analysis for studying the chemical composition and microstructure of the coating being sputtered onto Al - foil by EB – technology allowed to find out that the coating composition and its nanostructure depend on the technological parameters: substrate temperature, evaporating intensity, the sputtering angle of vapor current, working vacuum indicator, deposition rate, nitrogen content, etc.

Further R & D activities to create a CF new generation

The accomplished investigations did show that the basic properties of EB-CF including its thickness are noticeably better than the same of ECE- CF. Additionally, the conducted study lets ascertain an interesting fact that the Al cleanness indicator in an initial foil ceases to be important in the case for the EB-technology. It means that lower Al – cleanness grades as well as Al – alloys can be utilized for CF that finally decreases the cost expenses.
A special attention has to be paid to the fact that the research work done has put forward a number of interesting and important tasks. The solution of the latter will permit to overcome a very critical problem of the stability both the technological process itself and, as a consequence, the physic-technical characteristics given for the coating to be sputtered on the both surfaces of moving Al – foil.
In this connection the key criteria for R & D activities have been formulated. At present the work to meet the requirements defined is under implementation.
The criteria are the following.

At first, the search for opportunities to control the technological process permitting to forming a possible maximum share of TiN in the films and, consequently, increasing surface area of the coating deposited keeping in mind the interlinks between sputtering temperature, gaseous content in the working chamber, nitrogen supply rate, supporting an optimum Ti : N correlation.
Besides, the study how to control the EB- process with a view of maximum diminishing the presence of drops in the coatings sputtered, which worsen the development of coating surface area, are also under implementation stage.
The solution of the above technical tasks will allow to achieve an actual stability for the given parameters on SC, the TiN & oxides content in the coating, etc.

C o n c l u s i o n

1. A new ecology-safe technology to produce high capacitance cathode foil by EB – depositing onto Al-foil nanostructured coating with a highly developed surface area designed for the capacitors both oxide-electrolytic and with conducting polymer electrolyte was elaborated.

2. EB - cathode foils (EB - CF) are of much better basic quality characteristics in comparison with conventional CF made by employing an ecology unsafe electrochemical technology for etching (ECE - technology) Al foil as substrate to get developed surface areas (please, see Table 1). Besides, the thickness of EB - CF is up to twice thinner than ECE – CF that meets the modern demand to miniaturize electronic technique.

3. The experimental capacitors with EB – CF as a cathode have the indicators of "Leakage current" and "Dissipation factor" considerably lower than those standard characteristics for conventional capacitors with cathode made of ECE– CF (please, see Fig.3).

4. The result of research investigations made has shown that the EB – CF is of micro- and nanostructured coatings containing {Ti+TiN+Ti-oxides} films leading to forming highly developed coatings surface areas which finally gives high physic-mechanical characteristics for both CF and capacitors.

5. The research work done have been utilized to formulate R&D aims for present and future activities to further upgrading cathode as well as anode foils.

The scientists and researches, that have created the advanced EB – technology for CF and been keeping on developing new technologies and equipment to produce higher quality both cathode and anode foils, do hope that the work/information reported could be of some use for specialists/experts in electron technique in giving us invaluable advices in applying our materials science findings in practice.

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