RECOVERY OF AGED ANODE WIRES IN PROPORTIONAL COUNTERS USING A NEGATIVE CORONA DISCHARGE IN 80 % CF_4 + 20 % CO_2

G.E. Gavrilov, A.G. Krivshich, D.A. Maysuzenko, A.A. Fetisov, N.Yu. Shvetsova

1. Introduction

During last few years, large-scale studies of the radiation hardness of gaseous detectors were carried out in preparation for LHC experiments. Today, most of the factors affecting the aging rate of these detectors are well defined [1].

The "classical aging effects" are the result of chemical reactions occurring in the avalanche plasma near anode wires leading to formation of deposits on the electrode surfaces. This mode of aging is extremely sensitive to various additives and contaminants in the gas and materials used in contact with the gas. The most harmful chemical element, which is systematically detected in analyses of wire deposits, is silicon. Si compounds are found in gas-system components, sealant Room Temperature Vulcanizing Silicone Rubber, silicon-based lubricant, *etc*. Usually, Si deposits appear at the accumulated charges much below 1 C/cm per wire. That is why most of the materials used for construction of the detectors have to be tested to address their safety from the aging point of view.

Due to the need for radiation hardness, a broad list of conventional working gas mixtures was narrowed down to Ar(Xe) + CO_2 + CF_4. These mixtures block the negative influence of silicon deposits, preventing the anode aging. However, at the accumulated doses above 1 C/cm per wire, there exist aging effects that are not related to polymerization.

Anode wires are commonly made of gold-plated tungsten. It has been found that oxygen and other active radicals produced in avalanches penetrate through the pores and micro-cracks in the gold-plating and react with tungsten [2]. This process results in swelling of the wires because the forces within a wire break the gold-plating, and tungsten oxides (WO_x) appear on the wire surface. The aim of the present work was to demonstrate recovery of an aged anode wire in a proportional counter by treating it with a negative corona discharge in a 80 % CF_4 + 20 % CO_2 gas mixture.

2. Test set-up

Aging tests of straw-tubes were carried out using three ^{90}Sr β-sources mounted in a line with a total rate at one straw of 15 MHz. The beam profile of the irradiated zone was uniform with the width about 35 mm. Two straw-tubes used in our investigations had 0.4 cm diameter, and the anodes were made of 50 μm gold-plated tungsten wires. The gas flow rate was 0.5 cm^3/min, which was equal to four straw volumes per hour. To avoid both air and water vapor penetration into the straws from the outside, a set of straws was placed in a sealed box blown over by argon. Measurements of the straw tube properties were performed regularly each day after every charge accumulation increment of about 0.13 C/cm during the exposure [3, 4].

To monitor the gas gain, the photo peak position of a collimated ^{55}Fe *X*-ray source (E_γ = 5.9 keV) in the amplitude spectrum was measured at different test points along the irradiated straw. During the aging tests, we chose several working points of the high voltage to achieve gas gains and irradiation currents over a wide range: 2×10^4, 5×10^4, 1×10^5 and 0.38 μA/cm, 0.97 μA/cm, 1.98 μA/cm, respectively. This has covered the gas gains commonly used in gaseous wire detectors.

An analysis of the anode surface after the aging procedure was performed using a scanning electron microscope with *X*-ray emission (0–10 keV) spectroscopy (SEM/XEM).

3. Aging test results

Usually after accumulation of the total charge of about 1.5–1.8 C/cm at the rate of 0.13 C/cm per day, the wire degradation resulted in the gas gain reduction of about 10–15 %. The results of the SEM/XEM analysis of the aged anode wire in the centre of the irradiated zone (the gas gain being $G = 5 \times 10^4$) are presented in Fig. 1. As one can see, the gold coating was broken, and the tungsten oxide compounds

penetrated through the cracks in the gold layer and almost covered the surface of the swollen wire. As a result, the wire diameter increased by 6 % from 50 to 53 μm.

In principle, one known way to clean the wire surface from Si compounds and extend the operational lifetime of a straw detector non-invasively is to etch the wires by using a high current gas discharge in gas mixtures with CF_4 [5, 6]. We have applied this technique to WO_x cleaning, too.

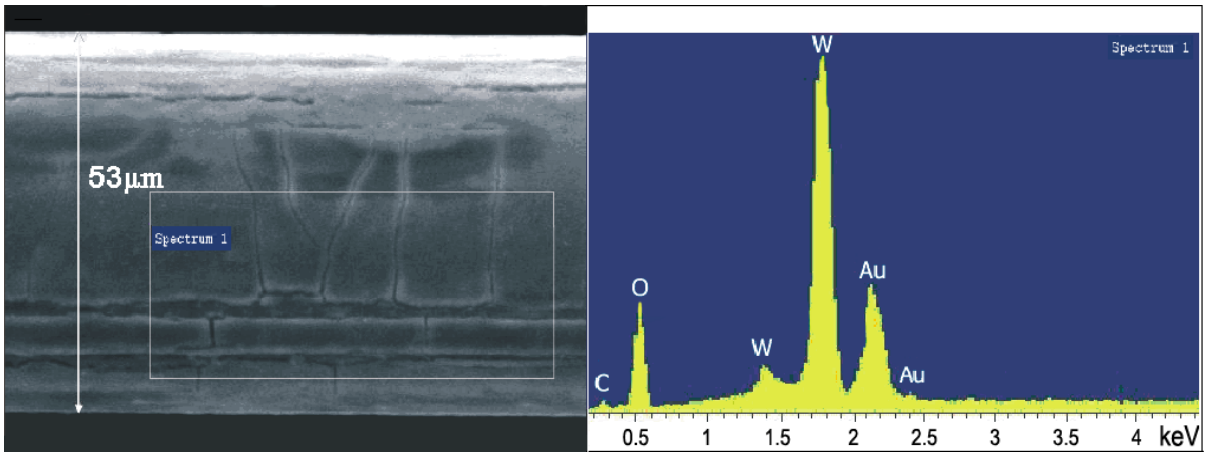

Fig. 1. SEM micrograph of the anode wire surface in the centre of the irradiated zone after the charge accumulation of Q = 1.53 C/cm (left) and XEM spectra (right) of the area that is denoted at the SEM micrograph by the rectangle

4. Task-setting

4.1. Glow discharge and integrated circuits production

Plasma chemistry is extensively applied in fabrication of semiconductor devices for microelectronic industry, which typically makes use of a glow discharge, which represents a low-pressure (< 1 Torr, RF-13.6 MHz) plasma. The glow discharge (DC, RF-plasma) in CF_4/O_2 gases is widely used in integrated circuits production for etching of silicon and tungsten compounds [7–9]. Our idea was to use this experience for removing tungsten oxides from the anode wire surface.

4.2. Corona discharge in wire chambers

The dominant parameter of a wire chamber is a strong non-uniform electric field around an anode wire. A classical corona discharge occurs in gases in regions of high electric field near sharp corners, edges of metal surface, including small diameter anode wires of MWPCs under atmospheric pressure. A start of a corona discharge in a straw (or MWPC) manifests itself with a sharp current increase.

It was observed that the gaseous products formed in avalanches in a proportional counter are qualitatively the same as expected under assumption that the chemical mechanisms in the avalanches are similar to the mechanisms of a low-pressure glow discharge [10–14]. On the other hand, because of strong non-uniform electric field around an anode wire, the spatial dimensions of the zone where chemical radicals, associated with the glow discharge processes are generated, is small and, according to our evaluation, does not exceed several tens of microns.

That is why it is important to find experimental evidence that the negative corona discharge can generate a considerable amount of chemical products usually associated with the glow discharge, which is enough to carry out effective etching of silicon and tungsten compounds in a proportional counter. If it is so, then one can use the principles of traditional plasma chemistry of a glow discharge (low pressure, RF) to predict the plasma chemistry of a corona discharge in the wire chambers (at 1 atm, DC).

5. Recovery of the aged anode wires

The wire etching is a rather complex chemical process. To obtain a general picture of the wire etching, it is necessary to identify the dominant processes occurring in the gas phase and at the gas/surface interface, resulting in formation of active chemical species (radicals, ions, *etc*.). The avalanche environment is plasma of ions and neutral radicals, and thus the wire etching process should be studied in the framework of the plasma chemistry. The intensity of ion and radical production depends on pressure, power density, detector irradiation rate, electric field strength, gas gain, materials of electrodes, gas composition including the presence of *ppm*-level impurities, *etc*.

5.1. Choice of the gas mixture

The discretion whether the etching or the yield of deposits will occur in CF_4 depends on plasma properties, although the F / C ratio model predicts that an effective etching gas mixture has the ratio of fluorine (F) to carbon (C) atoms in the range of $0.8 < F/C < 4.0$, and strong etching takes place at $F/C = 4$ [11]. On the other hand, the etching ability of tungsten compounds is more effective in CF_4/O reactive etching plasma [7–9]. To prevent the damage of carbon coating on the straw (cathode) wall during the recovery treatment, the oxygen in the etching gas mixture was replaced by CO_2. The needed oxygen radicals were mostly generated due to dissociation of CO_2 in collisions with the avalanche electrons near the wire. To optimize the recovery processes, the following gas mixture was chosen: 80 % CF_4 + 20 % CO_2 with the ratio $F/C = 3.2$ [15].

5.2. Etching process

The glow discharges media used in the plasma processing are partially ionized gases containing ions, electrons and neutral species in both ground and excited states. The degree of ionization is small, typically about 10^{-5} of all species, but the degree of dissociation can be quite large, sometimes exceeding 10^{-1} of all the species. Because of their higher concentration, neutrals (radicals) are the primary chemical species responsible for deposition and etching processes.

Due to a significant difference in mobility between the ions and electrons, the surfaces in contact with plasma generally acquire negative potential with respect to the plasma. As a result, positive ions are accelerated to the surface, and they can have a synergistic effect on the etching chemistry. This process is distinctly different in a wire chamber operating under atmospheric pressure, where the ionized gas contains electrons with a moderate energy of 5–10 eV, low-energy negative ions < 1 eV, and near-thermal positive ions [11].

To etch the tungsten or silicon compounds in a glow discharge (DC, RF-plasma), a negative potential was applied to the substrate that was in electric contact with the wafer. The etching process was carried out at a normalized electric field of 10–50 V/cm · Torr. The molecular dissociation leading to neutral radicals can be attributed to electrons with the energy in the range of 4–6 eV.

In a wire chamber (with a corona discharge, at 1 atm), the normalized electric field in vicinity of the wire surface is about 300–400 V/cm · Torr, which is enough to accelerate electrons up to the energy 5–10 eV. This energy is sufficient to break chemical bonds of the gas molecules and to start both molecular dissociation and other processes associated with the etching processes in a low-pressure glow discharge.

The mechanism of the etching process development can be considered to have four sequential steps:

- generation of active radicals $F^{\bullet}$, $O^{\bullet}$, $CF_3^{\bullet}$ in the gas discharge;
- their penetration through the wire gold coating;
- chemical interaction between the absorbed radicals and the wire materials leading to formation of tungsten compounds and their deposition on the wire surface;
- chemical interaction between the absorbed radicals and tungsten compounds leading to formation of volatile components and their desorption from the wire.

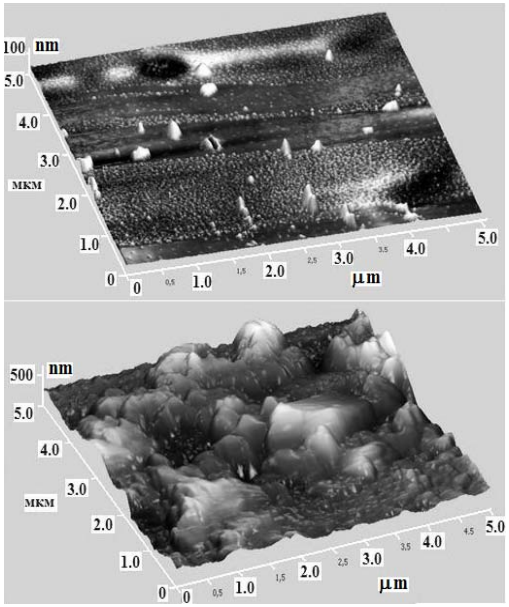

Fig. 2. Scanning Force Microscopy (SFM, solvent P47, cantilever HA-NC) images of both the non-irradiated wire surface (top) and the aged wire surface after irradiation (bottom)

To make the corona discharge recovery processes more stable, the damaged zone of the wire was irradiated with a low intensity 3.5 kHz ^{55}Fe *X*-ray source. Photons effectively stabilize the ionized plasma, supporting the etching conditions and breaking chemical bonds of the compounds coating the wire.

The wire surface in the centre of the irradiated zone is the main source of ionizing electrons because it is covered with irregular spikes of 100–400 nm height with the radii smaller than 1 μm, Fig. 2. The electric field on the tops of the spikes can be estimated as $E_{\max} \approx 2U/r \cdot \ln(2R/r)$, where $r \sim 0.5$ μm is the spike radius, $R = 2000$ μm is the straw radius, and $U \approx 2700$ V is the applied high voltage. As it follows from this formula, the electric field on the wire surface is about $E \approx 2.5 \times 10^5$ V/cm, and at least two orders of magnitude higher on the top of a spike, $E \sim 10^7$ V/cm. Therefore, a layer of tungsten oxides can be an additional source of electron current due to high field emission. Of course, such a wire surface damage stimulates micro-discharges and fast rising up of the corona discharge current, which results in production of radicals and ions in the vicinity of the wire surface.

The electrons formed in the ionized gas move in an intense electric field and obtain sufficient energy to break chemical bonds of the gas molecules. Thus, due to electron impact dissociation of CO_2 (the dissociation energy is $E_d = 5.5$ eV) and CF_4 around the anode wire, oxygen ions and radicals are produced, and many different active species, as well:

$$e^- + CF_4 \rightarrow CF_3^- + F^\bullet; \quad (1)$$

$$e^- + CF_4 \rightarrow CF_3^\bullet + F^\bullet + e^-; \quad (2)$$

$$e^- + CF_4 \rightarrow CF_2^{\bullet\bullet} + 2F^\bullet + e^-; \quad (3)$$

$$e^- + CO_2 \rightarrow CO^\bullet + O^\bullet + e^-. \quad (4)$$

The reactive gas fragments are transported in the electric field to the wire surface where they can be absorbed. The etching refers to a complex set of sequent chemical processes in which the gas-phase species interact with the tungsten-oxide compounds, which are placed both inside of the gold coating cracks and over the wire surface, the volatile products (↑) being evacuated through the gas. The most important plasma-chemical reactions for our gas mixture and their corresponding active radicals are the following:

$$W + O^\bullet \rightarrow WO_x\downarrow; \quad (5)$$

$$2WO_x + 10F^\bullet \rightarrow WF_6\uparrow + O_2\uparrow + WOF_4\downarrow; \quad (6)$$

$$2WOF_4 \rightarrow WO_2F_2\downarrow + WF_6\uparrow; \quad (7)$$

$$3WO_2F_2 \rightarrow WF_6\uparrow + 2O_2\uparrow + 2WO\downarrow; \quad (8)$$

$$WO \rightarrow W + O^\bullet; \quad (9)$$

$$W + 6F^\bullet \rightarrow WF_6\uparrow. \quad (10)$$

The average energy of positive ions in the gas discharge is almost thermal due to multiple elastic collisions with surrounding atoms and molecules. In contrast to electrons, ions do not store the energy obtained in the electric field: it is lost in each collision. The optimal etching conditions are fulfilled mainly in the peaks of the tungsten oxide compound where the electric field is high enough.

5.3. Choice of the working point for the negative corona discharge treatment

As it was mentioned above, a corona gas discharge occurs in high non-uniform electric fields surrounding anode wires. The tungsten-oxide deposits, which are placed both on the wire surface and inside of the cracks of the gold layer (see Fig. 2), will stimulate fast rising up of the corona discharge current because of their sharp shapes. Just in these points, chemical radicals generation associated with glow discharge processes becomes maximal, which results in intensive plasma-chemical etching of the tungsten-oxide peaks. As a result, the current of corona discharges falls down in time. That is why we performed the high voltage regulation every 30–40 min to compensate corona current decreases from 5 to about 1 μA.

In order to achieve the maximum etching rate, it was necessary to increase the current of corona discharges as high, as possible. This forced us to use a negative corona discharge because it has the following advantages in comparison to a positive corona discharge:

- this discharge is more stable and, consequently, it can generate a higher current;
- the mobility of negative ions is only half of that of positive ions.

Usually, the corona discharge in a straw manifests itself as a sharp current increase from 20–50 nA at the HV = –2500 V to 4–6 μA at the HV = –2650 V. The last potential was taken as the working point in the beginning of the recovery procedure.

5.4. Experimental results of recovery of aged wires

The progress of the wire recovery in terms of the gas gain along the straw is shown in Fig. 3a, b. Since the ^{55}Fe source spectrum has a sufficiently narrow peak in the 80 % CF_4 + 20 % CO_2 gas mixture, it was used to monitor the gas gain during the recovery process. The efficiency of the wire recovery procedure is presented in Fig. 3a. Such measurements were carried out every two hours. The gas gain distribution measured with the regular working gas mixture (60 % Ar + 30 % CO_2 + 10 % CF_4) before and after the recovery procedure is shown in Fig. 3b. As one can see, after six hours of the negative corona discharge treatment, the gas gain along the wire becomes the same as it was before irradiation.

Figure 4 shows results of SEM/XEM examinations of a restored anode wire surface in the centre of the irradiated zone in comparison with a non-irradiated wire surface. The total accumulated charge on a wire was 3 C/cm.

These results lead us to the conclusion that the proposed wire recovering procedure is very promising. The following processes are associated with the etching occurring after application of this procedure:

- the etched wire surface in the centre of the irradiated zone looks smooth and without any traces of deposits (tungsten-oxides compounds);
- the cracks formed by tungsten-oxides compounds in the gold layer (Fig. 1) have tightened. It means that etching of tungsten-oxides compounds occurs not only on the wire surface but also inside of the cracks and underneath the gold layer, too;
- the swollen wire diameter has decreased from 53 μm to the nominal value of 50 μm.

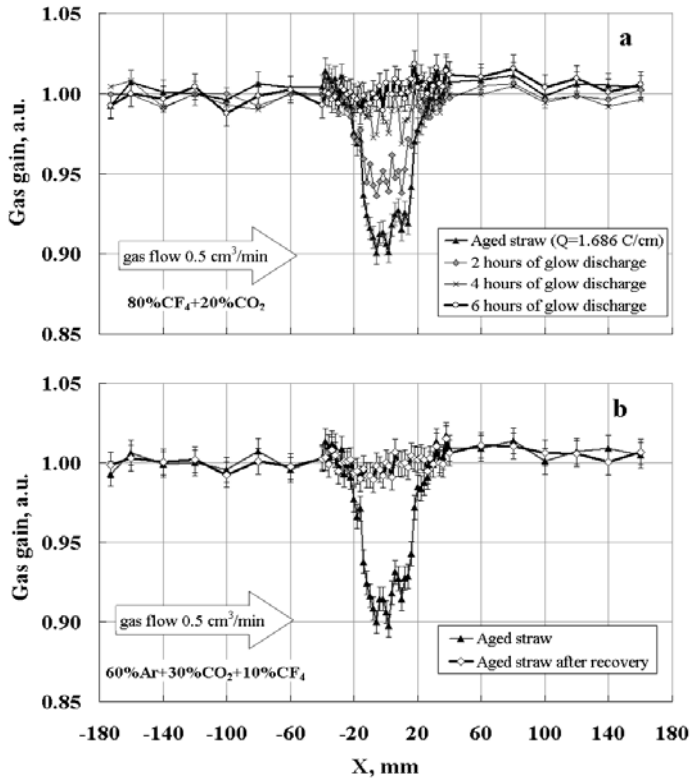

Fig. 3. a – gas gain behaviour along the straw during application of the wire recovering procedure. These measurements were carried out every two hours; 80 % CF_4 + 20 % CO_2 gas mixture, negative corona discharge; b – gas gain distribution along the straw before and after application of the wire recovering procedure; 60 % Ar + 30 % CO_2 + 10 % CF_4 working gas mixture

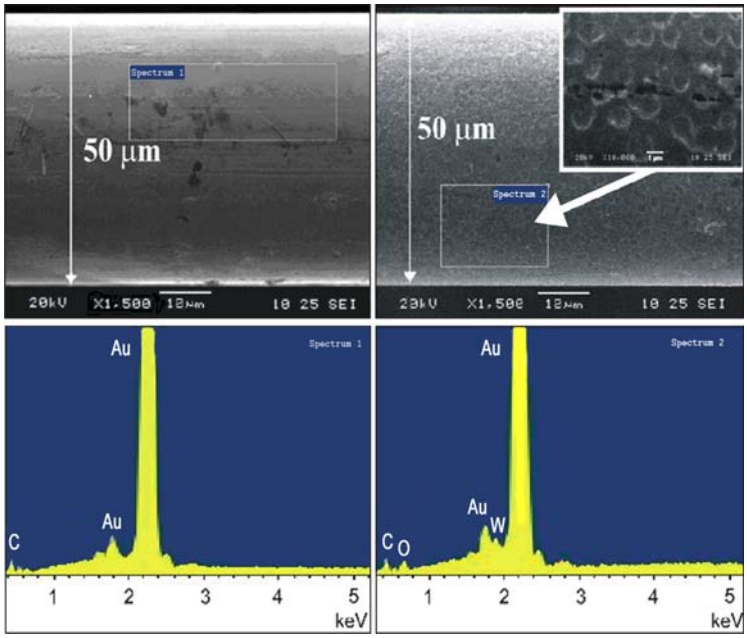

Fig. 4. SEM micrograph and the corresponding XEM spectra of the non-irradiated part of an anode wire surface (left) and in the centre of the irradiated zone of the wire after applying of recovery procedures (right). Both XEM analysis areas are denoted at the SEM micrograph by rectangles

6. Multiple recovery of aged anode wires

In order to confirm both the reliability and the reproducibility of the wire-recovering processes, multiple recoveries of the anode wires were performed. Our aim was to realize several cycles of an "aging-recovery" sequence during the continuous session of measurements.

The wire aging was carried out with a 60 % Ar + 30 % CO_2 + 10 % CF_4 gas mixture, and the recovery procedure was performed with an 80 % CF_4 + 20 % CO_2 mixture.

Two "aging-recovery" runs were performed. In the first run, the degradation of the gas gain in each cycle was 3 %, and in the second run in each cycle it was 6 %. During the first run, four cycles of the "aging-recovery" session were carried out, and during the second run three cycles were done. The total charge accumulated in each run was 3 C per 1 cm of the wire length.

The obtained data clearly demonstrate the efficiency of the proposed wire recovery method, see Fig. 5. As one can see, the application of a negative corona discharge to aged wires allows us to restore initial characteristics of a wire chamber several times. In other words, the lifetime of a straw detector can be increased by a few times. It is especially important when the wire detector is intensively irradiated with the irradiation current of about 1 μA/cm.

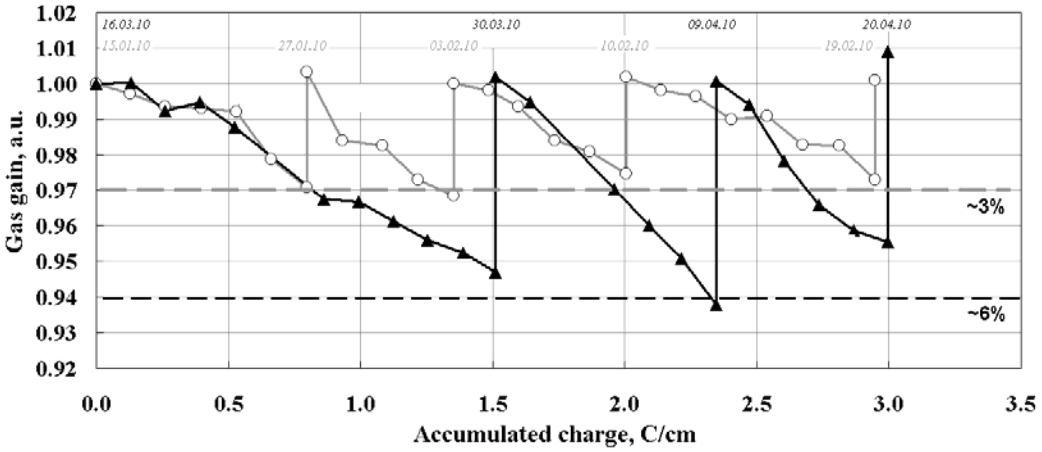

Fig. 5. Relative gas gain in the irradiated zone *vs* accumulated charge per unit of the wire length. The grey curve corresponds to the "aging-recovery" session with about 3 % of the maximum amplitude drop. The black curve corresponds to the "aging-recovery" session with about 6 % of the maximum amplitude drop due to wire swelling

Results of SEM examinations of anode wire surfaces in the centre of the irradiated zone after four cycles of "aging-recovery" session are shown in Fig. 6. As one can see, the wire surface is almost smooth and practically undamaged. Only some traces of WO_x compounds were found on the wire surface. This result looks almost similar to that of once-recovered wire, see Fig. 4. The wire diameter has decreased to the nominal value of 50 μm.

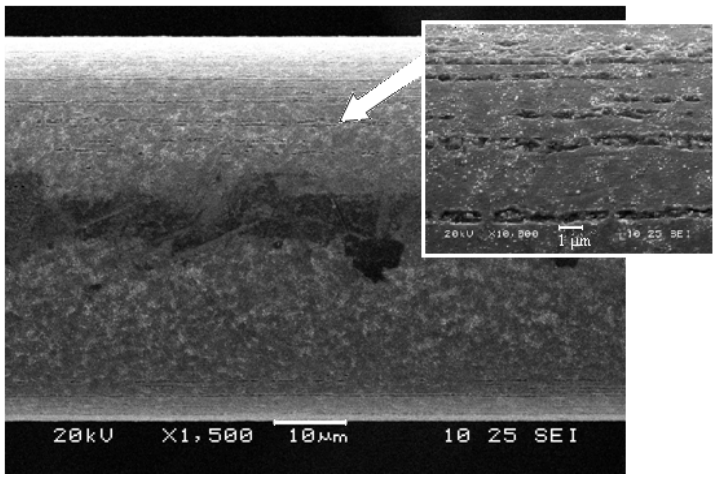

Fig. 6. SEM micrograph of the wire surface after applying of four cycles of the wire recovering procedure (see Fig. 5). The "aging-recovery" session with about 3 % of the maximum amplitude drop. The total accumulated charge was about 3 C/cm

7. Conclusion and outlook

1. A method for recovery of swollen anode wires in proportional counters by using a negative corona discharge treatment (with the current density about 3 μA per cm of the wire length) in 80 % CF_4 + 20 % CO_2 gas mixture has been proposed, successfully developed and tested. This method can remove from the surface of anode wires tungsten containing deposits which are accumulated there due to swelling effects.

2. Using this method, we have been able to recover a swollen wire multiple times, extending significantly the detectors lifetime. The proposed recovery mechanism is running "softly" and reliably.

3. We suppose that the application of the proposed method is more effective at the beginning of the detector degradation, when the gas gain drop does not exceed several percent (up to 9 %), and the total accumulated charge is smaller than 2 C/cm. For more aged wires, the wire degradation process becomes irreversible because of a high risk of formation of blisters and even ripping off fragments of the gold coating from the wire surface.

4. All the mentioned above experimental results allow us to conclude that the negative corona discharge can generate a considerable amount of chemical products usually associated with the glow discharge, which permit to carry out an effective etching of tungsten compounds in a proportional counter. This means that the principles of the traditional plasma chemistry of the glow discharge (low pressure, RF) can be used to explore the plasma chemistry of the corona discharge in wire chambers (1 atm, DC).

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