Electrical Characterization of Antistatic Coatings on the Neck Glass of Colour Cathode Ray Tubes

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The investigations of fluctuations of electrostatic potential in the cylinder of electronic optical system of colour cathode ray tubes induced by charge coupling on the surface of glass were performed. It is shown, that charge coupling and migration processes could be controlled by application of antistatic coatings. The sol-gel technology was applied for the formation of the antistatic coatings on the glass neck of CCRT. Different optically transparent oxide coatings compatible with the high temperature technological processes were deposited and tested. The measurements of the conductivity of coatings produced in different conditions were performed.
Keywords: electronic optical system, CCRT, antistatic coating, sol-gel

1. INTRODUCTION

Electronic optical system (EOS) of colour cathode ray tube (CCRT) is one of the main tube component that forms three accelerated electron beams directed to the screen matrix [1 – 3]. In CCRT electron trajectory towards the flat panel is influenced by magnetic as well as electrostatic fields, used for controlling electron beams, also the fields created by surrounding objects, e.g. the Earth magnetic field, electric and magnetic fields of near CCRT located elements or a field of static charge self acumulated on the surface of dielectric details of CCRT (e.g. on the surface of CCRT neck cylinder glass). High potential gradient (up to $2 \cdot 10^7$ V/m) between the electron optics electrodes induces strong electric fields not only inside EOS but also around it. These fields polarize nearby dielectric (the glass of neck cylinder) and can cause inevitable ion movement of alkaline metals (K, Na). (The main glass constituents used in CCRT neck production are SiO_2 (48.9 %), PbO (33.2 %), K_2O (10.3 %), Na_2O (2.2 %) etc.) Due to slow drift motion, other relaxation processes of electrostatic field in dielectric environmental conditions, like air humidity, temperature, near CCRT situated objects, have generous influence on surface charge fluctuations. Fluctuating charges in dielectric volume and surface produce chaotic oscillations of electrostatic field strength in EOS environment. At the same time fluctuations of electric field near the electronic optics influence electron beams trajectories, also focussing beams in CCRT screen matrix, which defines stability of colours.

On the other hand many different technologies [4 – 9] based on spraying technologies, sol-gel, dip coatings, spin coating etc. are used to produce transparent conducting oxide coatings for different fields of applications: use as electrodes in displays, solar cells, heating elements or in the provision of electromagnetic shielding or antistatic properties. The most commonly used materials in these fields are tin doped indium oxide, fluorine doped tin oxide, antimony doped tin oxide and aluminium doped zinc oxide.

In between of variety of methods liquid film coating is found at low cost and flexible deposition [10]. This technique offers deposition of sol-gel coatings inside tubes, though this technique offers a convenient and low-cost alternative to obtain high quality coatings.

In the present study electrical measurements were applied to identify critical parts for the charge phenomena on the neck of CCRT and to control electrical properties of the antimony doped tin oxide sol-gel coatings produced on the inside and outside surfaces of the neck.

2. EXPERIMENTAL

2.1. The measurement of electrostatic field potential distribution

Taking into account specifics of measuring conditions (complicated geometry of investigated object requires good surface resolution), the method of vibrating electrode was chosen [11 – 14]. Principles of operating of a special electrostatic voltmeter are demonstrated in Fig. 1. The amplitude of electrical signal in a resistor R is proportional to the difference of potentials between the investigated charged surface (surface under test) and the reference surface. This signal is registered by the electrostatic voltmeter. Electrostatic voltmeter by TREK INC firm with modified probe was adapted for the measuring. Schematic of the measurement equipment is shown in Fig. 2. In order to reduce the influence of surrounding objects on the measurements and enlarge surface resolution of the measuring equipment, the electrostatic voltmeter probe was placed into the ground connected screen, in which a small inlet was left at the measured zone. The diameter of

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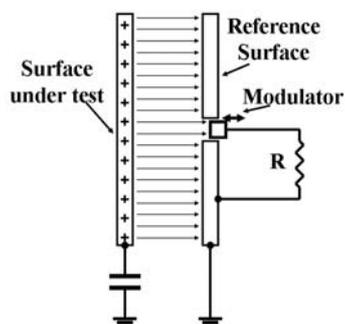
Fig. 1. Principle of operation of vibrating probe electrostatic voltmeter
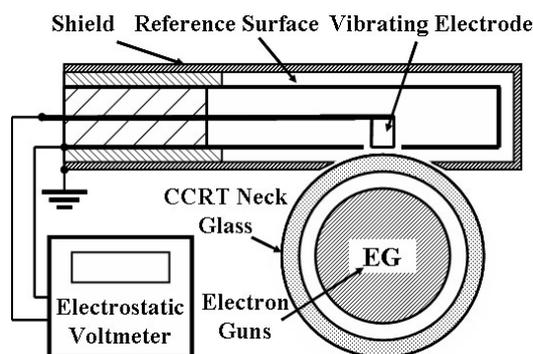
Fig. 2. The schematic of measurement equipment

measured zone didn't exceed 4 mm. The sensitivity of device was changed according to the measured potential. Such an approach enabled us to evaluate the distribution the potential along CCRT neck cylinder and its fluctuation in time.

2.2. The measurement of antistatic coatings resistance

A special probe system connected to the teraohmmeter E6-13A was produced for measuring the resistance of antistatic coatings formed on the CCRT neck glass by sol-gel technology. The scheme of measuring circuit is presented in Fig. 3. General view of the desk is shown in Fig. 4. Such system allowed to measure resistances up to $10^{13}\,\Omega$ of internal as well as external coatings of the cylinder. The spacing between probes was 5 mm.

The measurements were performed scanning the probes along a cylinder axis (x direction, Fig. 3). The results were registered every 10 millimetres. The measurements were taken three times, turning the cylinder around its axis every 120°. Using such method the coating homogeneity was tested controlling electrical conductivity along the cylinder and around the cylinder.
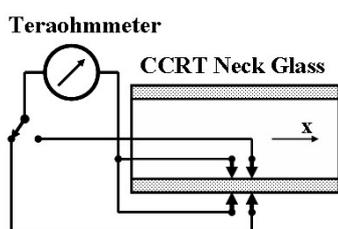
Fig. 3. The schematic of resistance measurement
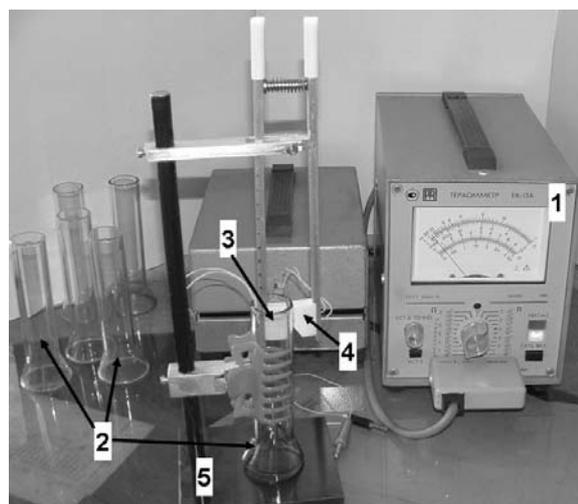
Fig. 4. Surface antistatic coatings resistance measuring desk: 1 – teraohmmeter, 2 – cylinders of CCRT neck, 3 – internal probe holder, 4 – external probe holder, 5 – the stand

2.3. Formation of antistatic coatings by sol-gel method

For formation of low electrically conductive optically transparent coatings on CCRT neck glass cylinder, a sol-gel technology was adapted. According to this technology colloid solution was prepared where water and alcohol as a solvent and metal chloride or metal nitrate as precursors were used. Later the surface of CCRT neck cylinder was coated by dipping reaching the electrically identified critical points. After drying the layer, it was heated up to 550 °C for 15 min. Fig. 5 shows the scheme [15] of this process.
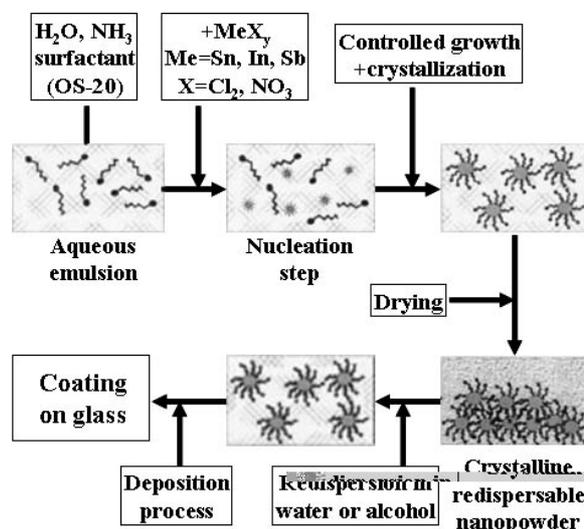
Fig. 5. Process scheme used to produce oxide coating on glass

After testing different solutions of MeX_y (Fig. 5) the only antimony doped tin oxide films was found to be compatible with the following high temperature procedures of CCRT (cutting, melting, etc). To optimize stability of the coatings different solutions have been tested.

Ethanol based solution of $SnCl_2 \cdot 2H_2O$ and water based Sb chlorides and nitrates were applied to produce coatings. The corresponding chlorides and nitrates were

produced mixing the Sb water solution with the mixture of HCl, HNO_3 and H_2O (Table 1).

Table 1. Solutions to produce antimony doped tin oxide layers

Solutions	$SnCl_2 \cdot 2H_2O$, ethanol		Sb metal (1.22 g/100 ml), (50 ml HCl+30 ml HNO_3 + 20 ml H_2O)
	Concentration, g/l	Volume, ml	Volume, ml
1	1	200	60
2	3	200	60
3	5	200	60
4	10	200	60
5	10	250	2

3. EXPERIMENTAL RESULTS

The relaxation processes of electrostatic field potential along the CCRT electronic optics axis at the external wall were analyzed by the vibrating probe method. While measuring probe was being moved along the CCRT neck in 5 mm steps and voltmeter readings were registered. After switching on the CCRT, the measurements were performed every 20 minutes. Fig. 6 presents the experimental results of electrostatic field potential distribution on the external side of the neck along the electrons guns axis (the scale factor for Fig. 6a and Fig. 6b is the same). The first curve corresponds to the potential distribution 20 minutes after switching on the CCRT, the second – after 40 minutes and the third – after 80 minutes. As it is seen, the surface potential of the CCRT neck not protected with the coating changes several (up to 4) times during 80 minutes. The biggest fluctuations for all CCRT investigated were noticed for the first 40 minutes. Later fluctuations in time decreased and stabilized at average value, what is depicted by a solid line (av).
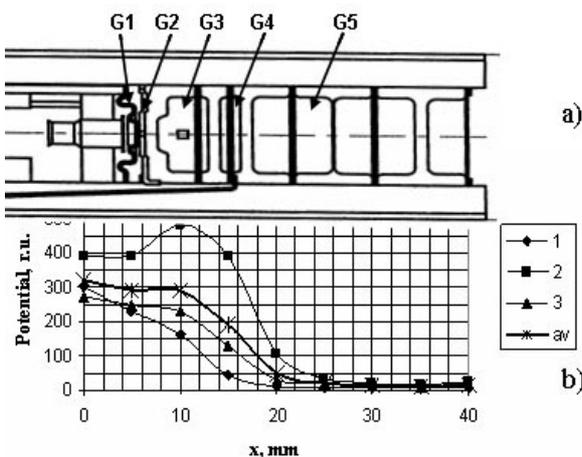
Fig. 6. Schematic of electron gun electrodes (a) within a CCR tube and corresponding potential changes on the external side of the cylinder along the axis (b): 1 – 20 min. after switching on the CCRT, 2 – 40 min., 3 – 80 min., where G1-G5 are the electrodes of EOS

Potential changes along the cylinder axis in all investigated CCRT demonstrate similar regularities. The highest potential gradient along the axis is observed in the accelerating and focusing (G3-G5) electrode zones. Because of the potential gradient in this zone there should be high longitudinal electric field, which would challenge surface charge drift. The highest fluctuations in time were noticed in the G2-G5 electrode zone. From these investigation results we can make a conclusion that in this zone exactly it is expedient to use antistatic coatings which could help to stabilize field potential fluctuations due to random oscillations of surface charge density.

Electrically conductive antimony doped tin oxide coatings formed by sol-gel method were deposited in the region of discussed critical points (thickness of the coating 100 nm). The coatings, produced using low concentration solutions (till 5 g/l) $SnCl_2$ (solutions No 1 and No 2, Table 1) demonstrated too low conductivity. Their layer resistance was of $10^{11} – 10^{13}$ Ω order. The electron beam convergent stability in the corresponding tested CCRT samples didn't improve. Testing different coatings it was determined that surface charge fluctuations started to decrease if antistatic layer resistance did not exceed 10^{10} Ω. Having enlarged $SnCl_2$ concentration to 5 g/l the first positive results were obtained. The best results were obtained using solution No 4. For high concentrations of $SnCl_2$ surface resistance became law ($R < 10^8$ Ω) and electric breakdown in operating CCRT were detected. Changing concentration of the solutions it was found that optimal surface resistance is $10^8 – 10^{10}$ Ω.

a

b
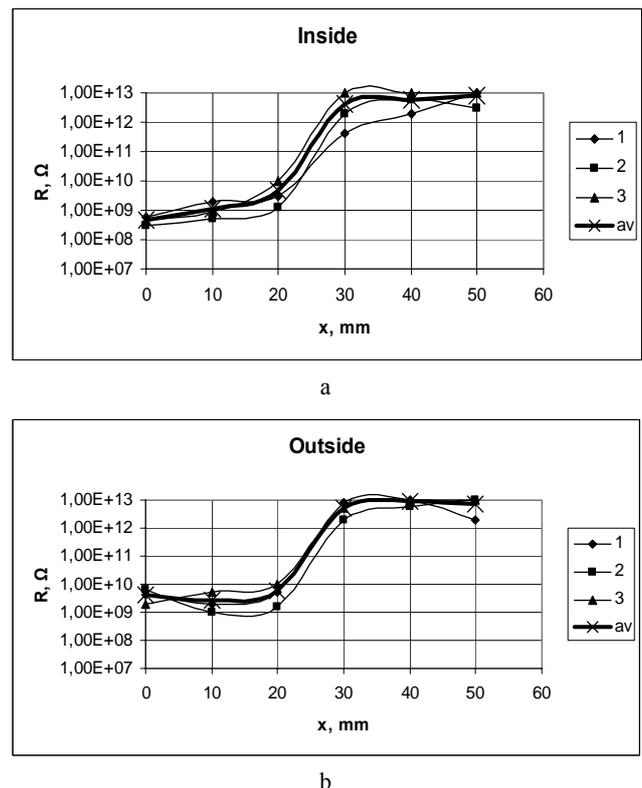
Fig. 7. Antistatic layer resistance along EOS cylinder: a – inside the cylinder, b – outside the cylinder. The curves 1, 2, 3 present resistance of the layer, measured turning the cylinder around its axis every 120° and the "av" presents average value of layer resistance

Fig. 7 presents resistance measuring results of the layer obtained from the solution No 4. The curves 1, 2 and 3 present resistance of the antistatic layer, measured

turning the cylinder around its axis every 120°. The curve „av" corresponds to the average layer resistance along the cylinder axis.

Fig. 8 presents XRD pattern with corresponding Miller's indices of the layer formed using the solution No 4. One can see that SnO_2 film is formed on the external part of the neck [16]. Comparing resistance on the inside and outside surfaces (Fig. 7) one can assume that the same coating is formed inside of the tube as well.
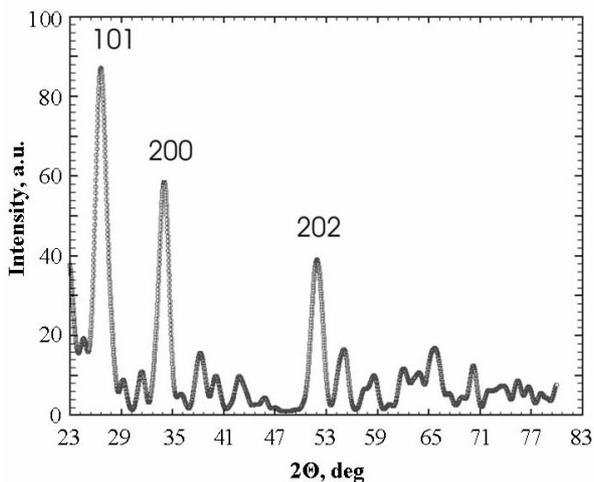
Fig. 8. XRD pattern of the SnO_2 antistatic layer ($d = 100$ nm)

One layer formation with increased tin concentration was efficient to produce stable layer with typical resistance $10^{10}\,\Omega$ that are compatible with the following CCRT technological steps. According to the preliminary data having used such type of coatings in the tested CCRT samples allowed to improve electron beam convergent stability.

5. CONCLUSIONS

1. Investigation of electrostatic field potential distribution near the external CCRT neck surface showed that the highest changes along EOS axis are in the vicinity of the accelerating and focusing electrode zone (G3-G5). In this zone namely it is expedient to deposit antistatic coating.
2. Tin oxide film doped with antimony formed by sol-gel method best sustains strict technological conditions of CCR tubes production.
3. Having produced CCRT testing samples with the antistatic coatings on the neck cylinders, it was determined that optimal antistatic coating resistance is $10^8 - 10^{10}\,\Omega$. Trying to establish optimal conductive layer in one layer concentration 10 g/l $SnCl_2$ with 4 g/l antimony in sol-gel solution is required.

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