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Metal-dielectric black matrix for display devices

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Abstract. Technology of metal-dielectric coating deposition for manufacturing a light-absorbing black matrix on a panel of color cathode-ray tubes is described. The coating is prepared using thermo-vacuum evaporation of SiO-Cr mixture. That yields in a thin-layer non-uniform (by its composition) structure SiO_x-Cr. It is shown that the coating prepared in this way is achromatic and has low reflectivity (~1%) from the side of a transparent panel. The index of diffuse light scattering measured for such metal-dielectric coating does not exceed 0.1% in the spectral range of 400-700 nm.
It is shown that black matrix based on the SiO_x-Cr coating can be produced using methods of direct or lift-off photolithography, with organic or non-organic photoresist. Color cathode-ray tubeswith these metal-dielectric black matrixes on their panels have increased image contrast as compared with the colloid-graphite ones.

Keywords: color cathode-ray tube, light-absorbing matrix, non-organic photoresist.

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1. Introduction

Despite the great interest to new generations of electronic display devices (liquid crystal, glow- discharge displays, vacuum fluorescent displays with field-emitter arrays), color cathode-ray tubes (CRT) hold their dominating position. Further development of them are going along the line of improvement their light-technical parameters. Positive results can be reached here by different ways: elaboration of more perfect construction of electron-optical systems, using new phosphorous with increased emission efficiency [1]. Particularly, an effective way of improving image quality on color screen is creation of a black matrix (BM) on it (less common term is «light-absorbing matrix»).

On color CRT panels and diverse types of displays the interspaces between separate phosphor (luminous) elements are filled by light-absorbing black coating, thus forming a BM that absorbs external light and a scattered radiation from adjacent elements. As a result, the black matrix provides a distinct tone for each color pixel of the display as a whole and makes the more contrast color image.

At present, the coatings based on high-dispersed colloid-graphite compositions are used to form BM in color CRT. Colloid-graphite layers are deposited by spin-coating method, then dried and patterned by lift-off photolithography. But the characteristics of colloid-graphite coatings (diffuse reflectance, thermal stability, mechanical strength and adhesion to glass) not always satisfy the demands to BM.

Known also is the method of producing BM based on coatings prepared in the course of consequent vacuum evaporation of metal oxide and metal layers, where metal is Cr or Ni. Such two-layer coatings are rather dark and patterned by the method of direct photolithography, using positive photoresist. Another way is in using a laminated film, deposited by RF-sputtering [2]. The laminated film includes a transition layer comprising at least one metal constituent element whose content increases along an incident direction of external light. The metal constituent element is selected from the group consisting of chromium, tungsten, tantalum, titanium, iron, nickel, and molybdenum, a second constituent element selected from the group consisting of oxygen, nitrogen, and carbon. But such coatings can be deposited only in flat display production line (for example LCD). The practical utilization of these methods in color CRT production is limited in view of the relatively complex methods of metal-oxide layer production (e-beam, RF-sputtering).

This paper reports our investigations of more simple method of BM producing by thermal vacuum evaporation. According to this method, spatially inhomogeneous metal-dielectric (SiO_x-Cr) films is deposited, using standard vacuum aluminizing posts of color CRT production line, and patterned by lift-off or direct photolithography.

2. Deposition and characterization of a black coating

The low reflection from the facial side of a panel, high optical density and electric conductivity of a black coating (BC) are the most important parameters, which determine its suitability for BM manufacturing. In a thin-film coating (thickness less than 1 μm) such set of parameters can be obtained only in spatially inhomogeneous structures with the composition varying through the film thickness. At the smooth increase of refraction and absorption coefficients over the thickness of inhomogeneous film it is possible to receive an achromatic coating with high absorption and low reflectivity in a broad spectral range.

Samples for investigation were obtained by thermal vacuum evaporation at a pressure $(2...4)\cdot 10^{-3}$ Pa of dispersed powderlike mixture consisted of (x) wt.% SiO and (100-x) wt.% Cr onto glass substrate, or CRT panels. Parameters of the coatings mostly depend on the content of evaporated mixture and previous measurements showed that optimum values lie in the region $10 \le x \le 40$ [3]. Layer thicknesses were controlled «in situ» by the quartz microbalance technique and also measured using micro-interferometer MII-4. The total film thickness was in the range of 0.3...0.6 μm. The smooth increase in evaporator temperature led first to the evaporation of dielectric component, then the co-evaporation of both components, and finally the metallic component was involved. In the coating obtained in this manner, the component composition was continuously changed from the pure dielectric (SiO_x) through the intermediate region containing both components (SiO_x-Cr) to the pure metal (Cr).

Atomic content distribution through the thickness of coatings was ascertained using Auger spectrometer (VG MICROLAB 310-F).

Reflectivity of the coatings from the substrate side for the normal incidence of measuring light in the visible spectral range was measured using spectrophotometer KSVU-23 equipped with reflection attachment. Diffuse reflectivity for 45°-angle incidence and optical density of the coatings were measured using the standard SDI Co. technique.

Fig. 1 shows depth profiles of Cr, Si and O content in the coatings obtained by evaporation of $(SiO)_{30}Cr_{70}$ mixture. The depth distribution of constituent elements in the film is essentially inhomogeneous. The Cr content near substrate is less than 5% (the thin layer near the substrate consist mostly of SiO_x), but on the film surface it is more than 95%. In the transition layer the chromium content increases approximately by 3% per 10 nm.

The thickness of transition layer was approximately 300 nm, that of layer with high chromium content was 150 nm, and full coating thickness was 450 nm. Such coating had optical density more than 4 and sheet resistance (measured using 4-probe method) near 40 Ohm/□.

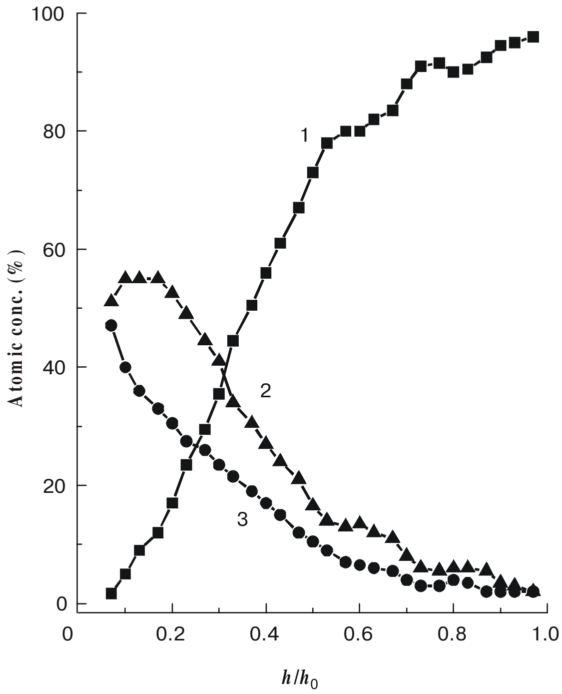

Fig. 1. The depth distribution of Cr (1), Si (2) and O (3) atomic contents in the inhomogeneous SiO_x-Cr coating. h_0 = 450 nm is the thickness of the coating, h is a distance from the glass substrate.

To investigate the depth distribution of optical and electrical characteristics of such inhomogeneous structure, we prepared a model sample. During evaporation of SiO-Cr mixture, the special mask with the slit was shifted step by step along the glass substrate in such way that vapors could be deposited only through the slit. The prepared set of narrow thin film strips represented the gradient of the composition along the substrate, which could be quantitatively investigated by standard optical and electrical techniques.

In Fig. 2 the profile of extinction coefficient (k) of the inhomogeneous SiO_x-Cr layer is shown. It is seen that when the composition changes from SiO_x to Cr the extinction coefficient is changed from zero to values typical for Cr films. This growth of k is accompanied by nearly linear change of refractive index from 1.6 to 3.1[4] and substantial change of sheet resistance (r) (Fig. 3).

Fig. 4 shows the spectral dependence of the mirror reflectance (R_{fs}) of the sample (inhomogeneous coating SiO_x-Cr on a glass substrate), measurements being carried out from the substrate side, R_s is a reflectance of the substrate-air interface. The reflectance of the coating ($R_f = R_{fs} - R_s$) is very low (~1%) in visible wavelength range that results in effective absorption of external light and scattered radiation. Besides, this coating has extremely low values of a diffuse reflectance (R_d = 0.05 – 0.1% in

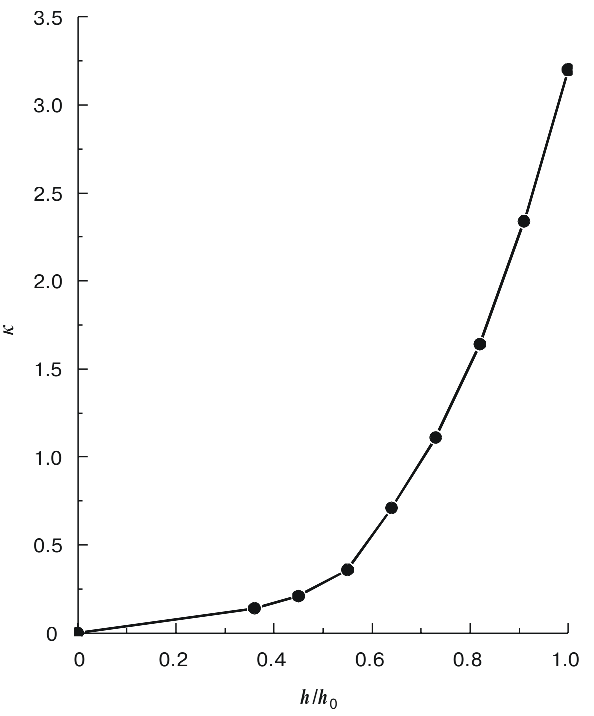

Fig. 2. The depth profile of extinction coefficient of the SiO_x-Cr layer. h_0 and h are the same as in Fig.1.

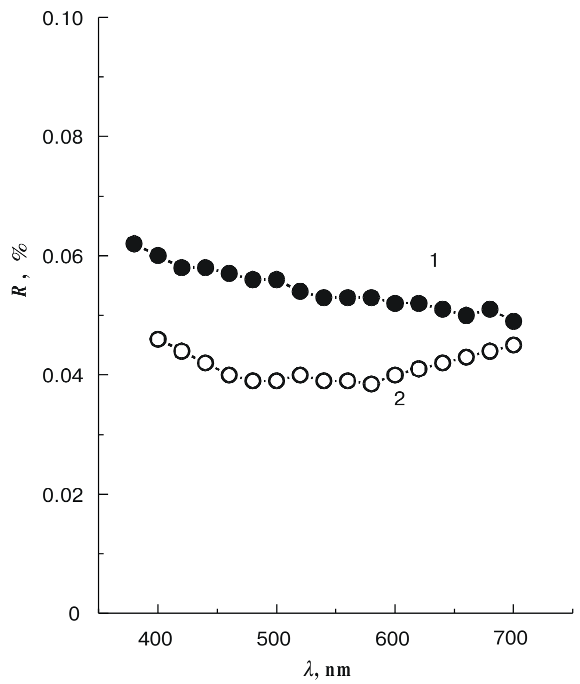

Fig. 4. Spectra of mirror reflectances measured for the SiO_x-Cr coating, R_{fs}(1), and the substrate-air interface, R_s (2). λ means a light wavelength.

visible wavelength range) (Fig. 5, curve 1), which increases the image contrast, too. These values do not change after thermal treatment during 1 hour at 450^{0}C which is determined by the technology of electron-beam tube production. For comparison, corresponding values of graphite coating are shown in Fig. 5, curve 2.

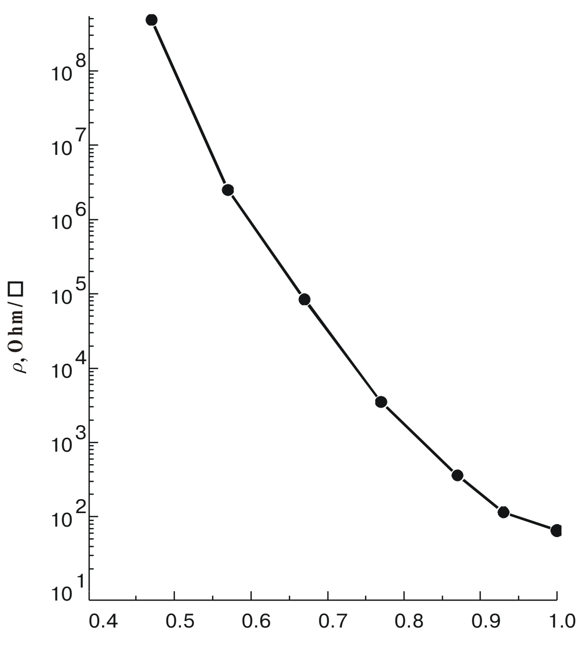

Fig. 3. The depth profile of sheet resistance of the SiO_x-Cr layer. h_0 and h are the same as in Fig.1.

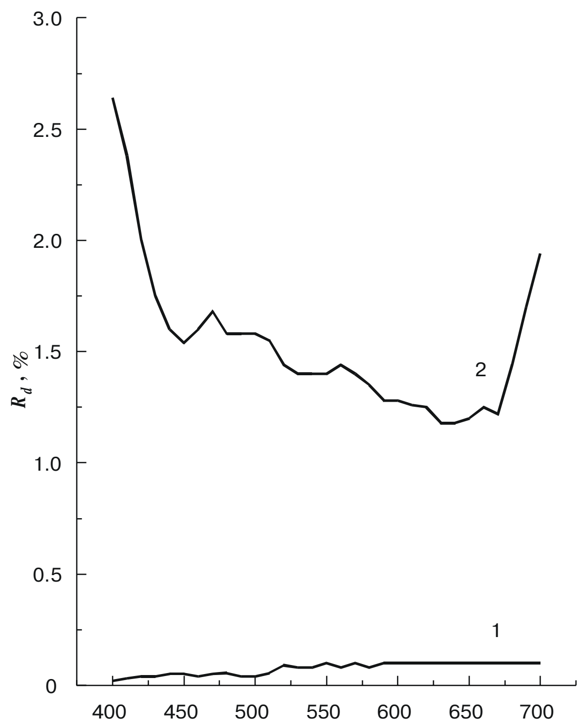

Fig. 5. The diffuse reflectance (R_d) spectra of SiO_x-Cr (1) and graphite (2) coatings.

3. Manufacturing black matrix

Owing to nonuniform component thickness distribution, SiO_x-Cr coatings can be dissolved using wellknown selective chemical etchants for Cr and SiO. It provides manufacturing BM by direct photolithography. Using this method, light-absorbing and photoresistive layers can be deposited sequentially in one technological route, which considerably increases efficiency of BM production and decreases matrix defectness. In traditional technology of manufacturing BM based on a colloid-graphite mixture, direct photolithographic process is impossible since chemical etchants for colloid-graphite preparation are unknown. By the contrast, metal-dielectric BM can be prepared by both photolithographical ways.

The method of direct photolithography was realized using positive photoresist AZ-HKT-501 in the following stages: thermo-vacuum deposition of black coating on an internal surface of a tube panel, spin-coating photoresist deposition, soft-baking of the obtained photoresist layer, exposing it and developing in a standard solution. These were followed by hard-baking the photoresist mask and etching the coating. Then the photoresist mask was removed.

Standard negative organic photoresist based on polyvinyl alcohol are unsuitable for patterning of metal-dielectric coatings. These photoresists are thermally unstable, and a photomask made of them can be easily destroyed when above it thermo-vacuum deposition of metal-dielectric mixture is applied. It was the reason that forced us to develop and use nonorganic photoresist based on chalcogenide glasses [5]. The main advantage of such photoresists is the possibility to apply thermo-vacuum deposition, too. They provide usage of both direct and lift-off lithography for BM production. However, application of non-organic resists is connected with some complication of technology and additional financial expenses.

Using the method of direct photolithography based on the positive photoresist AZ-HKT-501 we produced several samples of 6-inch panels with BM made of the metal-dielectric layer and investigated their performances. Photo fragment of such matrix is shown in Fig. 6. Such vacuum deposited black matrix has a number of advantages over the BM based on the traditional colloid-graphite composition:

- low values of diffusive light reflectance, an order of magnitude smaller than those of colloid-graphite layers;
- excellent physical and chemical properties (high values of mechanical strength, heat resistance, etc.) and stability under thermal and chemical treatment;
- nonhydroscopicity and absence of gassing;
- high reproducibility of properties under deposition.

The technology of SiO_x-Cr matrix fabrication is more productive, than the graphite one. It enables to increase a yield factor and output. Preliminary estimates have shown that the application of the new technology will not lead to increasing of CRT manufacturing cost. The comparison of the CRT with graphite and SiO_x-Cr matrixes has shown the essential advantages of the latter as to operation parameters. In comparison with the matrixless CRT the contrast of display with SiO_x-Cr matrix is increased approximately by two times while for the graphite matrix — only by 20%.

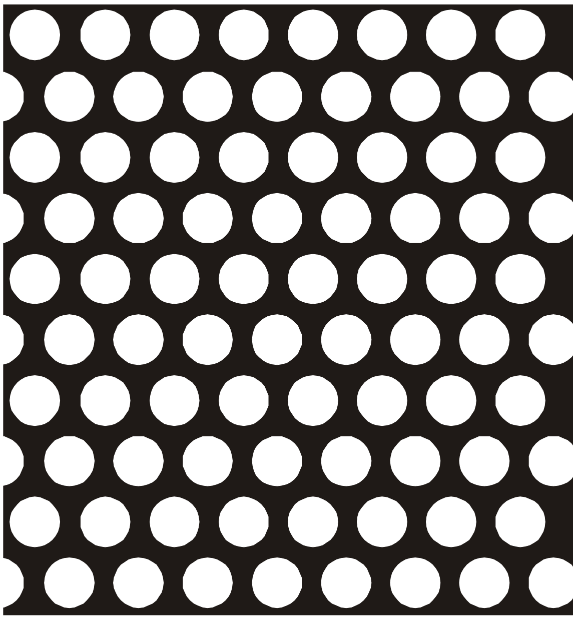

Fig. 6. Fragment of 6-inch panel with a black matrix made of the inhomogeneous SiO_x-Cr coating.

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