INVESTIGATION OF THE STRUCTURE AND CERTAIN ELECTRICAL CHARACTERISTICS OF CHROMOSILICON FILMS DURING HEAT TREATMENT

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Fixed metallized nonwire-wound resistors are one of the most massive types of parts in modern radio electronic equipment. Widely used as the conducting element in them are layers of chromosilicon having a high specific resistivity (of the order of $6 \cdot 10^{-2} \Omega \cdot \text{cm}$), a comparatively low temperature coefficient of resistance, TCR ($\pm 4-6 \cdot 10^{-4}$ per degree), and a high chemical resistance. The most important technological operation in manufacturing these resistors is heat treatment, during which the layers of chromosilicon acquire stable parameters.

In this work we investigated, by means of x-rays, the process of the formation of the crystal structure of chromosilicon films during heat treatment both in a vacuum and in air, and attempted to relate the structural changes with electrical changes (conductivity, TCR, and the Hall constant).

The chromosilicon films were obtained by volatilization of the alloy (24% Cr + 76% Si) in a vacuum of $10^{-4}-10^{-5}$ mm Hg with tungsten vaporizers, proposed by V. A. Bochkareva, on an unheated backing of fused quartz glass. The backings were prepared before spraying the layer by chemical cleaning and heating in a vacuum up to 400°C. Before applying the film bands were applied to the ends of the small cylinders in a vacuum, into which the platinum-silver contacts were later brazed.

The temperature dependence of resistance was investigated in a quartz tube placed in a muffle furnace. A vacuum of $10^{-3}-10^{-4}$ mm Hg was created in the tube. The x-ray structural analysis of the films was carried out in an RKD chamber with chromium radiation. The thickness of the films was checked by calculation and interference methods. Numerous measurements showed that the difference in layer thickness determined by these methods was not more than 10% (h = 0.1-0.4 μ).

The resistance of the specimens was measured by the null method by means of potentiometer EPP-09 and the Hall voltage by the dc compensating circuit. The tables given below and the curves were constructed from average values. The maximal deviation from the mean did not exceed 10-12%.

![Fig. 1. Dependence of TCR of chromosilicon films on annealing temperature.](image)

![Fig. 2. Change of conductivity of chromosilicon films during heat treatment: 1) in vacuum; 2) in air.](image)

The appearance of a uniform fog on the x-ray photographs obtained from films both freshly sprayed and those heat treated in a vacuum and in the air to a temperature below 350°C permitted the assumption that scattering of x-rays occurred from irregularly arranged structural elements of the film, i.e., that the chromosilicon films on heating to 350°C are amorphous or finely divided. According to Kramer's theory [1], metallic layers can be in an amorphous state only at thicknesses of the order of 0.01-0.02 μ. Since silicon films at all thicknesses examined in an electron microscope are amorphous, but chromosilicon films are not purely metallic and represent a rather complex composition of metal and silicon, the obtained data are quite real.

Further results of the process of structural formation upon heating of chromosilicon films in a vacuum are shown in Table 1. The holding time at each temperature was constant—10 min. At 350°C two lines, quite blurred and of low intensity, were noted. It was found that these are reflection lines from planes (111 and 003) and (103) of the CrSi₂ phase. At 400°C line (111) appears along with those present, whereas at 500°C the less intense lines of chromium appear. In this case the lines belonging to chromium disilicide are as usual diffused, whereas the lines belonging to chromium are not. This can indicate that the crystals of metallic chromium that formed are somewhat larger than the crystals of CrSi₂.

The increase of line intensity can be related to an increase in the number of CrSi₂ and Cr crystals. At 600°C the lines belonging to the phase of metallic chromium disappear, and the line intensity of the phase CrSi₂ increases, and lines of weak intensity, for example (110), even appear. Along with this appear lines belonging to crystalline silicon. We propose that the disappearance of metallic chromium in a free state is due to the additional formation of crystals of the CrSi₂ phase.

Upon heating to even higher temperatures (of the order of 750-800°C) the phase composition does not change but the form and width of the lines do, which can indicate enlargement of the crystals and removal of microstresses at higher annealing temperatures. We checked what caused the spread of the lines of the main phase. The assumption of a relation between the spread and the size of the crystals formed seems to be correct. The size of the crystals, calculated by the half-width of the lines of the microphotometer curve varies from 40-50 Å (at temperatures of 400-500°C) to 1000 Å (at an annealing temperature of 800°C). However, their size even on heating to 800°C is smaller than in the original alloy of chromosilicon.

Since the x-ray patterns of films heat treated up to 800°C was severely fogged, this enabled us to assume that even at high annealing temperatures the entire amorphous phase does not become crystalline. On the x-ray photographs obtained from films heat treated in air, we detected, in addition to the aforementioned lines, scarcely noticeable lines belonging to silicon oxides. These were lines (200) and (203) of the α-cristobalite phase of SiO₂ and line (101) of the α-quartz phase of SiO₂. The main phase of the chromosilicon films on heating both in a vacuum and in air is the compound CrSi₂, which agrees fully with the phase diagram [2]. Chromium disilicide crystallizes hexagonally, the unit cell, according to our