

Structure and optical properties of chromium layers evaporated at different rates on substrates of different temperatures

ELŻBIETA IDCZAK, LUCYNA KOŚCIELNIAK *

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

The influence of the evaporation condition, i.e., the deposition rate (1–50 Å/s) and the substrate temperature (35–600° C), on both the structure and the optical constants (0.2–25 μm) of the chromium layers has been examined. It has been stated that, if the suitable technology is used, the layers are of polycrystalline structure ranging from fine-grained (20 Å) for the layers evaporated on the unheated substrates to the coarse-grained (1000 Å) one for the layers evaporated on the substrates of temperature 600° C. No influence of the evaporation rate within the applied range on the structure of the obtained layers has been stated. On the other hand, a distinct influence of the substrate temperature on the coefficient of reflection and optical constants of chromium layer was observed.

1. Introduction

Optical properties of chromium layers have been examined in our laboratory for many years [1]–[3]. Recent examinations of the process of chromium layer oxidation at the oxygen atmosphere showed that the annealing of the chromium layers at the temperature of about 500–600° C causes probably some change of the structure of the obtained layers [4]. This fact provoked the examination of the influence of both the substrate temperature and the evaporation rate on the produced layer structure.

2. Production of the layers and calculation of the optical constant

The chromium layers were obtained in the NA 500 vacuum unit (produced by the Vacuum Equipment Works in Bolesławiec, Poland) by using the method of thermal evaporation. The preliminary material was the spectrally pure IMC 703 chromium. The layers were obtained from the tungsten basket at the vacuum of order of $1.33 \cdot 10^{-4}$ Pa (10^{-6} Torr) on the polished quartz plates and cleaved immediately before the evaporation on the NaCl substrate. The substrates were

* Present address: ul. Dzielna 23/17, 50-900 Wrocław, Poland.

annealed with a special heater [5] while the substrate temperature was measured in vacuum with the Pt-PtRh thermocouple. The substrate temperature was changed from the room temperature up to 600°C. The gettering process of the chromium was employed during the layer production in order to increase the layer purity [6], [7]. The layer deposition rate was changed from 1 Å/s to 50 Å/s. The thickness of the examined layer was of order of 150–200 nm and the substrate temperature in the evaporation process was subsequently equal to: 35°C, 200°C, 300°C, 400°C, 500°C and 600°C.

In order to produce the chromium layers under different technological conditions the reflection coefficient $R(\omega)$ has been measured in the broad wavelength range from 0.2 μm to 25 μm , for normal incidence of the light wave. Several spectrophotometers were exploited to cover this spectral interval.

In the visual spectral range (from 450 μm to 650 μm) for the same layers additional ellipsometric measurements Δ and ψ for two angles of incidence of the light wave (65° and 70°) were performed. From the ellipsometric measurements of Δ and ψ the optical constants of chromium layers n and k have been measured in the visual range [8], taking account of the fundamental equation of ellipsometry

$$\tan \psi e^{i\Delta} = \frac{\sin \varphi \tan \varphi}{\sqrt{(n - ik)^2 - n_1^2 \sin^2 \varphi}}$$

where: φ – angle of incidence of the light rays on the layer, Δ – phase difference between p - and s -components of the light reflected, ψ – azimuth of the reconstructed linear polarization.

The optical constants of chromium have been calculated in the wide spectral range (0.2–25 μm) by using the Kramers–Kronig method. The formula joining the amplitude and phase of the complex Fresnel coefficient in the case of normal incidence of the light has the following form:

$$\alpha(\omega) = -\frac{\omega}{\pi} \int_0^{\infty} \frac{\ln R(x)}{x^2 - \omega^2} dx$$

where: α – phase of reflected wave, R – coefficient of reflection. This formula allows to calculate the phase change at the reflection $\alpha(\omega)$ if the coefficient of reflection is known within the 0– ∞ frequency range. Since the measurements of $R(\omega)$ are always performed in a limited frequency range $\omega_1 \leq \omega \leq \omega_0$ the phase of the reflected wave may be written as

$$\alpha(\omega) = \alpha_k(\omega) + \Delta\alpha(\omega).$$

The first of these expressions

$$\alpha_k(\omega) = -\frac{\omega}{\pi} \int_{\omega_1}^{\omega_0} \frac{\ln R(x)}{x^2 - \omega^2} dx$$

is calculated numerically on a computer on the base of the experimental measurements of $R(\omega)$ [9].

In order to take account of the contribution of the phase of the reflected wave from the unmeasurable range of frequencies $\Delta\alpha$ a suitable extrapolation should be used. In paper [10], a detailed analysis of the $\Delta\alpha$ has been carried out and it has been stated that independently of the character of the changes of $R(\omega)$ within the frequency range $\omega_0 - \infty$ it is always a magnitude increasing monotonically with ω . Besides, the contribution to the phase of the reflected wave coming from $\Delta\alpha$ depends, above all, on the character of changes of the coefficient of reflection $R(\omega)$ in a very narrow frequency interval $\omega \leq \omega_0$. For the metals, for which there are no rapid changes in $R(\omega)$ within the frequency interval $\omega \simeq \omega_0$, which is our case, the expression $\Delta\alpha(\omega)$ may be calculated from the formula

$$\Delta\alpha(\omega) = B\omega \left[1 + \frac{1}{3}(\omega/\omega_0)^2 \right],$$

where

$$B = \frac{\alpha_{\text{exp}} - \alpha_k}{\omega},$$

B is here the average value calculated within the interval in which the phase may be determined by using another method [9]. In the present work, the phase α_{exp} has been calculated on the base of optical constants of the chromium layers obtained from the ellipsometric measurements in the visual spectral range.

Having measured experimentally the coefficient of reflection $R(\omega)$ and calculated the change of phase $\alpha(\omega)$ for the same spectral range

$$\alpha(\omega) = \alpha_k(\omega) + B\omega \left[1 + \frac{1}{3}(\omega/\omega_0)^2 \right]$$

the optical constants may be calculated from the following formulae:

$$n = \frac{1 - R}{1 + 2\sqrt{R \cos \alpha} + R}, \quad k = \frac{2\sqrt{R \sin \alpha}}{1 + 2\sqrt{R \cos \alpha} + R}.$$

The structure, phase composition and the texture of the chromium layers have been examined with the help of electron microscopy, of electron and X-ray diffraction.

3. Measurement results

The examinations carried out showed that the coefficient of reflection R for chromium layers depends distinctly on the substrate temperature T_s of the layers obtained. The values of the coefficient of reflection increase with increasing substrate temperature during the condensation of the layers for the whole (0.2–25 μm) spectral range. On the other hand, no dependence of the coefficient of reflection R for the chromium layers upon the deposition rate has been noticed

within the 1–50 Å/s range of the rates applied (Figs. 1 and 2). Also the optical constants n , k of the layer examined do not change with the change of deposition rate (Figs. 3, 4) within the range of the rates applied (1–50 Å/s). On the other hand, a distinct dependence of the optical constants of the chromium layers on the substrate temperature during their condensation has been stated. The coefficient of

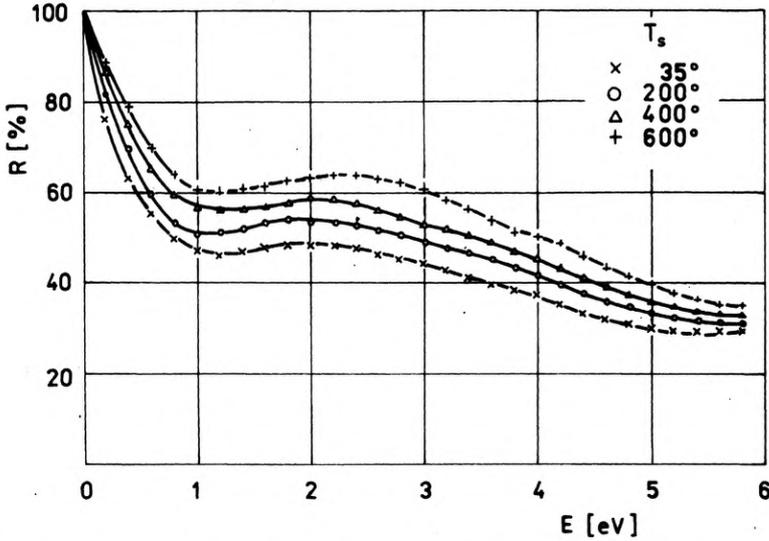


Fig. 1. Spectral dependence of the reflection coefficient R for the chromium layers evaporated at the rate $v \sim 1$ Å/s onto heated substrates of different temperatures T_s

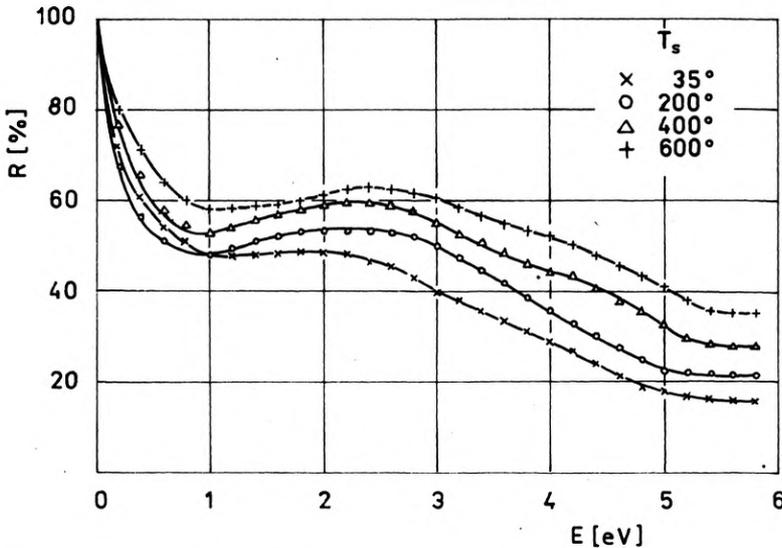


Fig. 2. Spectral dependence of the reflection coefficient R for the chromium layers evaporated at the rate $v \sim 50$ Å/s onto heated substrates of different temperature T_s

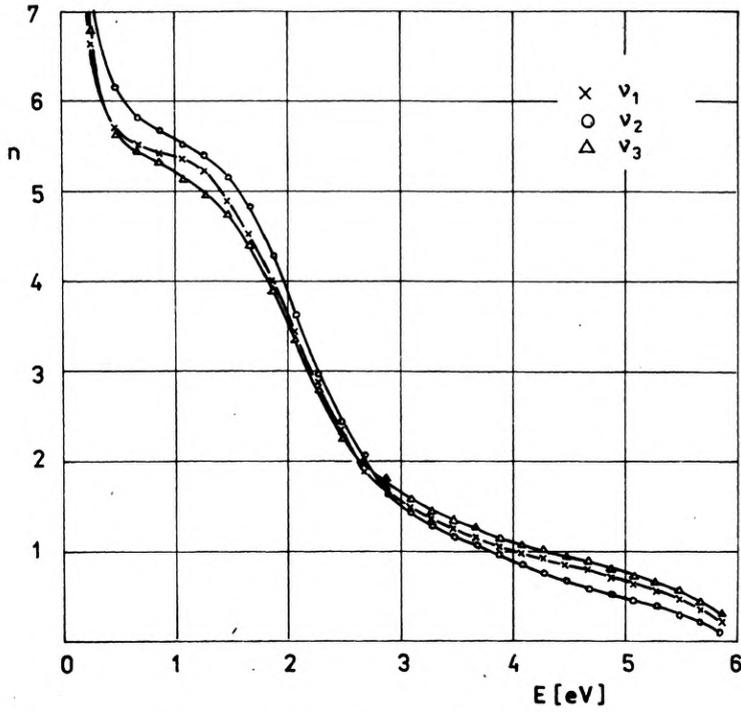


Fig. 3. Spectral dependence of the refractive index n for chromium layers evaporated at different rates at $T_s = 600^\circ\text{C}$

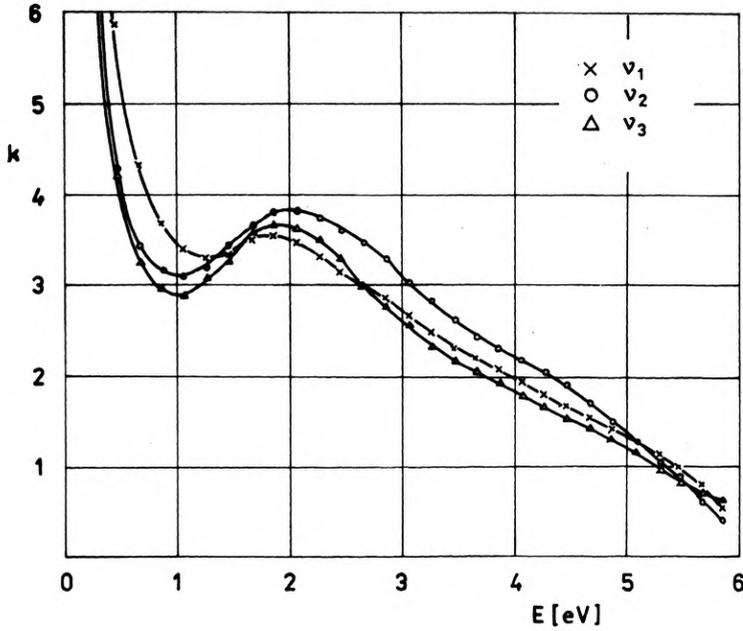


Fig. 4. Spectral dependence of the absorption coefficient k for chromium layers evaporated at different rates at $T_s = 400^\circ\text{C}$

absorption of the chromium layers increases for the whole spectral range with the increase of the substrate temperature while these changes are greater in the infrared and visual range than in the ultraviolet one (Fig. 5). The refractive index for the chromium layers increases also with the substrate temperature in the

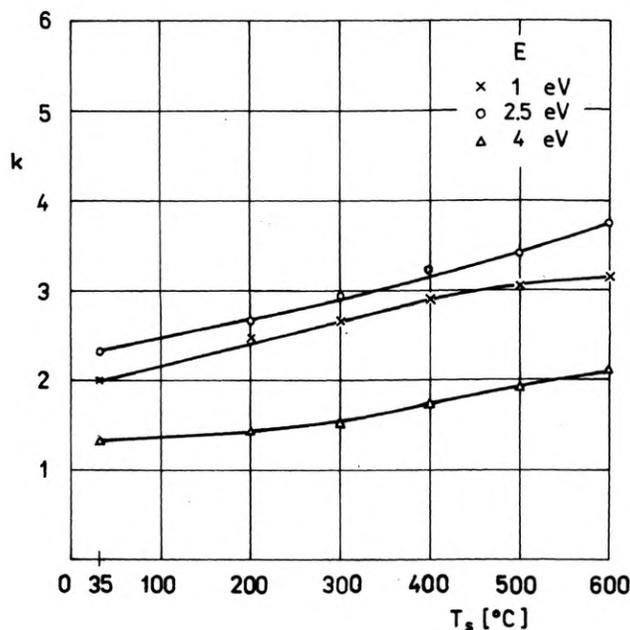


Fig. 5. Dependence of the absorption coefficient k from the substrate temperature T_s for the chromium layers evaporated at the rate $v \sim 50 \text{ \AA/s}$

Phase analysis of chromium layers

Sample number	v [\AA/s]	T_s [°C]	Diffraction lines [\AA]	Observed crystallographic phases
1	6.8	35	2.03	α -Cr*
2	7.4	200	2.04, 1.44	α -Cr
3	8.8	300	2.03, 1.44	α -Cr
4	7.4	400	2.03, 1.44	α -Cr
6	6.2	500	2.03, 1.44	α -Cr
7	4.8	600	2.04, 1.44	α -Cr
8	0.7	35	2.03	α -Cr
14	1.3	600	2.03, 1.44	α -Cr
31	10.6	35	2.03	α -Cr
22	30	35	2.03	α -Cr (b.c.c.)
			2.05	Cr (p.c.)**
41	44.4	35	2.03	α -Cr (b.c.c.)
			2.05	Cr (p.c.)

v – evaporation rate of the layers, T_s – substrate temperature during the layer condensation, * – metallic chromium (α -Cr form), elementary cell b.c.c. of regular body-centred cubic structure (Im3m), $a_0 = 2.884 \text{ \AA}$, ** – metallic chromium (polygraphic form), elementary cell p.c. of primitive regular structure (Pm3), $a_0 = 4.588 \text{ \AA}$.

infrared region while it slightly decreases with the substrate temperature in both visible and UV ranges (Fig. 6).

The structural examinations showed that the chromium layers produced by using the technology described above have the structure of regular body-centred cubic lattice (Im3m) – see the Table. Only in the layers evaporated at a high rate on the substrate of low temperature $T_s = 35^\circ\text{C}$ chromium was stated to appear in

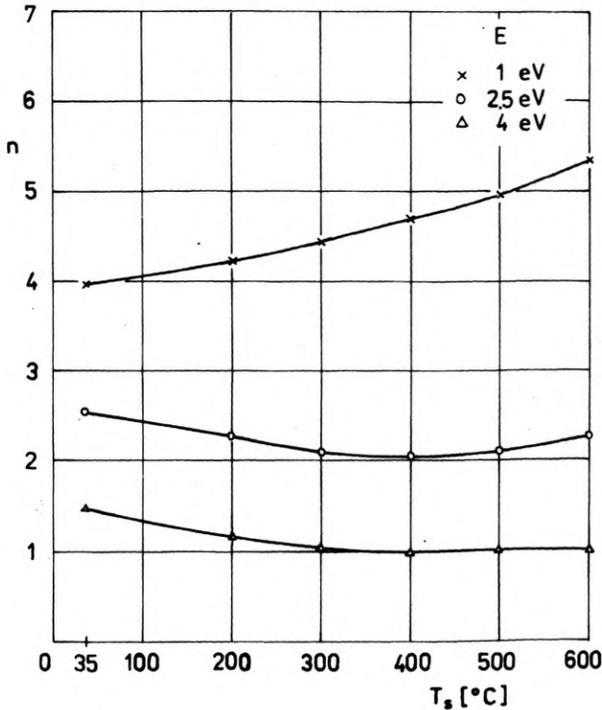


Fig. 6. Dependence of the refractive index n on the substrate temperature T_s for the chromium layers evaporated at the rate $v \sim 1 \text{ \AA/s}$

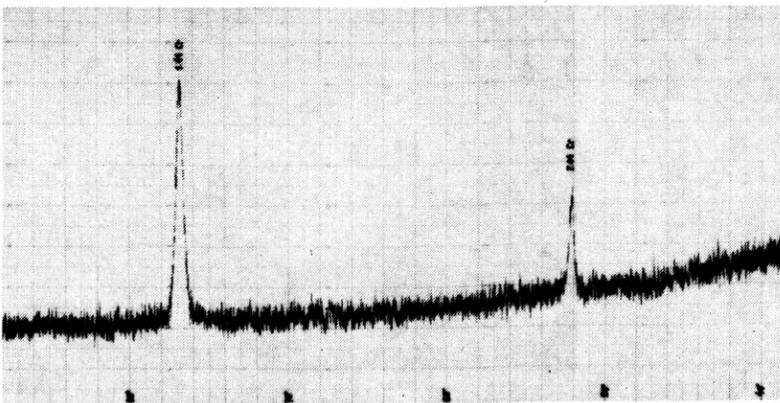


Fig. 7. X-ray diffraction of the layer ($T_s = 600^\circ\text{C}$, $v = 1.3 \text{ \AA/s}$)

two types of lattice: regular body-centred cubic lattice ($Im3m$) and regular primitive one ($Pm3$). However, the quantity of the latter form of chromium is much less than that of the first one. In the layers examined no oxygen bond of chromium has been stated. The texture of the layers changed with the substrate temperature. For the layers evaporated on the substrate of low temperature the orientation $\{110\}$ of the crystallites (texture) prevails, while for the layers deposition on the substrates of higher temperatures the texture $\{200\}$ occurs (Fig. 7).

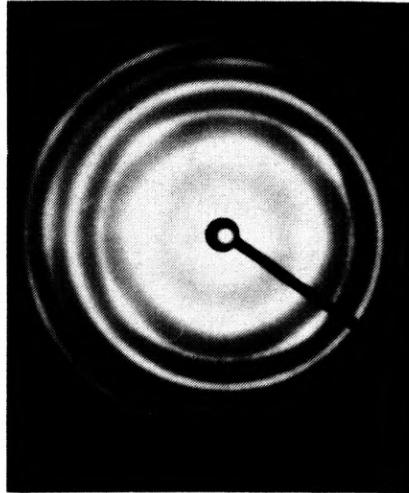
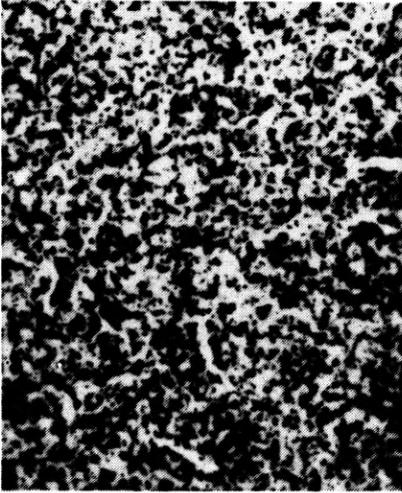


Fig. 8. Microstructure of the layer examined. Magnification $43,000\times$ ($T_s = 35^\circ\text{C}$, $v = 30 \text{ \AA/s}$)

Fig. 9. Electron diffractogram for the region in Fig. 8

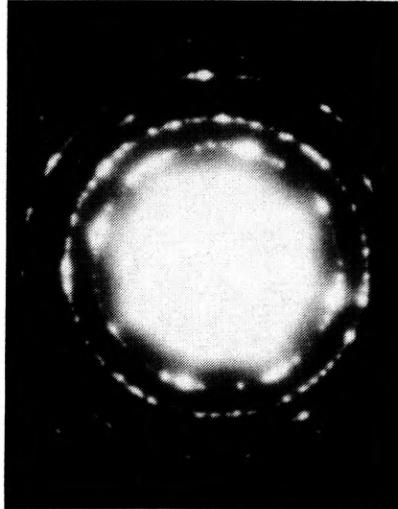
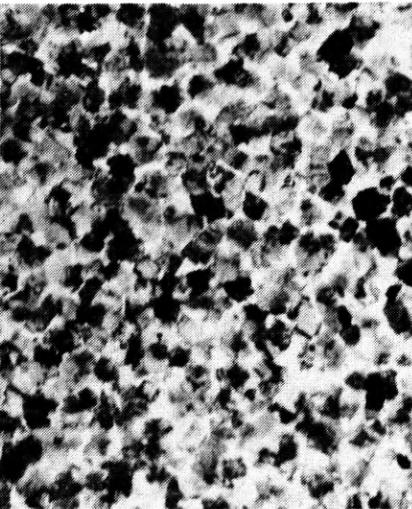


Fig. 10. Microstructure of the layer examined. ($T_s = 600^\circ\text{C}$, $v = 4.8 \text{ \AA/s}$)

Fig. 11. Electron diffractogram for region in Fig. 10

The application of the methods of electron microscopy and diffraction allowed to establish that the chromium layers examined are composed of small crystals adjacent to each other, the sizes of which depend upon the substrate temperature. The layers produced at the room temperature are built of very tiny crystals of sizes comparable with the resolving power of the microscope. It has been estimated that the crystals of these layers are of order of 20 Å (Figs. 8 and 9). On the other hand, for the layers deposited on the substrates of 600°C temperature the crystals reach the sizes from 700 to 1700 Å (on average 1000 Å), Figs. 10, 11.

4. Conclusions

From the examinations carried out it follows that in the vacuum of order of 10^{-6} Tr ($1.33 \cdot 10^{-4}$ Pa) the change of evaporation rate from 1 to 50 Å/s (no higher rates were available) does not influence the layer structure and by same means the optical properties of the obtained chromium layers. On the other hand, the substrate temperature is an important factor influencing the structure of the obtained layer. The layers deposited on the quartz substrate of temperature changing from room temperature to 600°C are of (Im3m) polycrystalline structure while the crystal sizes are the greater the higher the substrate temperature.

The chromium layers deposited on the substrates of higher temperatures exhibit both higher coefficient of reflection and higher and higher coefficient of absorption for the whole spectral range (0.2–25 µm). The refractive index of these layers remains practically constant within the visible and ultraviolet spectral range while it increases with the substrate temperature within the infrared region.

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References

- [1] IDCZAK E., Scientific Papers of the Institute of Technical Physics of Wrocław Technical University No. 7, Ser. Monographs No. 2, Wrocław 1973 (in Polish).
- [2] IDCZAK E., *Opt. Appl.* **3**, No. 2 (1973), 25.
- [3] IDCZAK E., *Optika i Spekr.* **15** (1963), 107 (in Russian).
- [4] IDCZAK E., OLESZKIEWICZ E., *Optika i Spekr.* **49** (1980), 570 (in Russian).
- [5] RACHWALSKA L., Doctor's Thesis, Institute of Physics, Technical University of Wrocław, Wrocław 1983, Poland (in Polish).
- [6] MIKHAILOV G. S., *Optika i Spekr.* **16** (1964), 176 (in Russian).
- [7] KOSTYUK V. P., SHKLYAREVSKII I. N., *Optika i Spekr.* **16** (1964), 305 (in Russian).
- [8] IDCZAK E., *Opt. Appl.* **3**, No. 2 (1973), 31.
- [9] IDCZAK E., RACHWALSKA L., *Opt. Appl.* **11** (1981), 307.
- [10] KIRILOVA M. M., NOMEROVANNAYA L. V., BOLOTIN T. N., MAEVSKII V. M., NOSKOV M. M., BOLOTIN M. C., *Fiz. Met. Metalloved.* **25** (1968), 459 (in Russian).

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Структура и оптические постоянные плёнок хрома, полученных на подложках с разной температурой и разной скоростью

Исследовано влияние условий возгонки, т.е. скорости нанесения ($1-50 \text{ \AA}/\text{с}$) и температуры подложки ($35-600 \text{ }^\circ\text{C}$) на структуру и оптические постоянные ($0,2-25 \text{ мкм}$) получаемых плёнок хрома. Установлено, что полученные в этих условиях плёнки хрома имеют поликристаллическую структуру от мелкозернистой (20 \AA) для плёнок, осажденных на неподогреваемой подложке, до структуры крупнозернистой (1000 \AA) для плёнок, осаждаемых на подложке с температурой $600 \text{ }^\circ\text{C}$. Не замечено влияния скорости осаждения (в диапазоне применяемых скоростей) на структуру получаемых плёнок. Однако установлено отчётливое влияние температуры подложки на структуру и оптические постоянные плёнок хрома.