Optical and electrical properties of very thin chromium films for optoelectronic devices

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Abstract. Establishing the optimal experimental conditions for the development of transparent metal contacts to be used in optoelectronic devices, such as organic light-emitting diodes and solar cells, is an important task. In this paper we present an overview of the development of very thin e-beam-deposited chromium films with high optical transparency. The surface morphology is investigated by scanning electron microscopy. The variation is examined of the films’ electrical and optical properties (transmittance and complex refractive index) with the variation of the thickness and deposition rate. We observed that, for a given thickness of the chromium films, the absorption coefficient increases when the deposition rate is decreased. We also found that the thin films with a thickness of less than 10 nm show an average transmittance exceeding 60% in the spectral range 400 – 1500 nm. The films’ resistivity, ρ, is determined by the four-point probe method. The value of ρ varies in the range of 10⁻³ – 10⁻⁴ Ω cm for chromium coatings in the thickness interval 5 – 100 nm. The results obtained show that very thin metal films could be an alternative to the transparent conductive oxides.

1. Introduction

Thin chromium films have found many applications, for example as layers for improvement of the adhesion to transparent substrates [1], in mask production [2] and as transparent electrodes [3]. Recently, it has been demonstrated that the ultrathin transparent metal contacts provide a number of advantages over the more commonly used conductive transparent metal oxides, such as indium tin oxide (ITO) [4]. According to [5], chromium and nickel thin films possess optical transparency comparable to that of the ITO in the visible and near-infrared range (0.4 – 2.5 μm), while it can be significantly higher in the ultraviolet (175 – 400 nm) and mid-infrared (2.5 – 25 μm) regions.

The conditions of deposition, as deposition rate, temperature of substrate, etc., influence very strongly the properties of the metal coating [6]. It has been shown that the deposition rate and argon partial pressure in the case of cathode sputtering strongly affect the microstructure and electrical properties of thin chromium films [7, 8]. Metal films deposited by ion-beam sputtering display exceptionally low surface roughness, the films being as thin as about 20 Å [3].

The goal of the present work is the investigation of the optical and electrical properties of very thin chromium films deposited by an electron-beam technique.

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2. Experimental details
Thin films of chromium were deposited by the e-beam technique in a Leybold-Heraeus A 702 Q thin films deposition system. The e-beam evaporation was performed in vacuum \( p \approx 3 \times 10^{-3} \) Pa at a deposition rate of 0.2 nm/s and controlled by a quartz monitoring technique. The thickness of the thin films was also cross-checked ex-situ by a Talystep profilometer.

The surface of the thin films was observed by a Joel Superprobe 733 (Japan) scanning electron microscope. The film’s resistivity, \( \rho \), was determined by the four-point probe method. The transmittance (\( T \)) and reflectance (\( R \)) were measured by a Cary 5E (Australia) UV–VIS–NIR spectrophotometer in the range 350 – 2000 nm to an accuracy of \( \Delta T = \pm 0.1\% \) and \( \Delta R = \pm 0.5\% \).

3. Results and discussion
The SEM image of a 15-nm thick chromium film is presented in figure 1. A smooth surface was observed for all thin films.

The transmittance spectra of thin chromium films deposited by e-beam evaporation are shown in figure 2. The values of \( T \) are lower at the shorter wavelengths and increase at higher \( \lambda \). It is seen that the films’ transmittance is above 65 % for thin films with a thickness of 10 nm. The thin film with a thickness of 5 nm exhibited transmittance in the range of 67 – 80 % in the visible spectral range and transmittance higher than 80 % in the near infrared range.

The refractive index, \( n \), the extinction coefficient, \( k \), and the film thickness, \( d \), were calculated from the transmittance or reflectance spectra as described in [9]. The method is based on minimization of the discrepancy between the theoretically calculated (\( T(\pi, \kappa, \lambda, d) \)) and \( R(\pi, \kappa, \lambda, d) \) and the experimentally measured values \( T_{\text{exp}} \) and \( R_{\text{exp}} \) of the transmittance and reflectance at normal incidence until the difference becomes lower than the accuracy of the measurements, \( \Delta T \) and \( \Delta R \) [10-11].

\[
\begin{align*}
T(\pi, \kappa, \lambda, d) - T_{\text{exp}} &= \Delta T \\
R(\pi, \kappa, \lambda, d) - R_{\text{exp}} &= \Delta R
\end{align*}
\]

Discontinuities appear in the solution for \( n \) and \( k \) due to the requirement for an accurate film thickness value, while there is loss of solutions at the critical points [12]. The thickness \( d \) is not computed from set (1), but is introduced as a parameter. For an initial approximation for the thickness we used the value measured by a profilometer with an accuracy of \( \pm 1 \) nm. Hence, by varying the thickness slightly around the approximate one, we chose the value yielding the smallest discontinuities in the solution for \( n \) and \( k \). The accuracy in the determination of the refractive index, \( n \), was better than \( \pm 0.005 \) and that for the absorption coefficient, \( k \), around the absorption edge was about \( \pm 0.01 \) [11, 13].

The real and imaginary parts of the complex permittivity, \( \varepsilon = \varepsilon' + i\varepsilon'' \), can be calculated from the refractive index and extinction coefficient by the following equations:

\[
\begin{align*}
\varepsilon' &= n^2 - k^2 \\
\varepsilon'' &= 2nk
\end{align*}
\]
The results for the refractive index, the extinction coefficient, and the real and imaginary parts of permittivity are given in figure 3. The decrease of the films’ thickness leads to a drop of the refractive index. The values of \( n \) are in the range of 2.5 – 3.5 for thin films with thickness 16 and 35 nm, while \( n \) varies from 1.47 to 1.64 for the 5-nm coating in the 400 – 1500 nm spectral range.

The trends in the variation of the imaginary and real part of the permittivity relative to the films’ thickness are similar to those of the refractive index. As is seen in figure 3d, the imaginary part of the complex permittivity, \( \varepsilon'' \), decreases as the films’ thickness is decreased.

The variation of the film’s resistivity, \( \rho \), is given in table 1. It can be observed that the value of the resistivity decreases for thicker films. A sharp increase of the values of the resistivity is observed for films thinner than 22 nm. The results for \( \rho \) are in the same order of magnitude as for the thin films deposited by cathode magnetron sputtering [14]. According to [15], the sheet resistance, \( R_s \), of ITO films with thickness 50 – 100 nm is in the range 2 – 6 kΩ/sq.

Taking into account that the relation between the real part of the conductivity, \( \sigma' \) and \( \varepsilon'' \) is

\[
\sigma' = \frac{1}{\rho} = \frac{\varepsilon''}{4\pi}
\]

where \( \sigma' = 1/\rho \) is the real part of complex conductivity and \( \omega \) is the angular frequency. It is seen from equation (3) that the imaginary part of the complex permittivity, \( \varepsilon'' \), is proportional to the conductivity. Consequently, the increase of \( \varepsilon'' \) with the thin films’ thickness (see Figure 3d) is related with the

**Table 1.** Resistivity of thin chromium films, \( \rho \), sheet resistance, \( R_s \) and their thickness, \( d \).

| Film thickness, \( d \) [nm] | \( \rho \) [Ω cm] | \( R_s \) kΩ/sq |
|---|---|---|
| 5 | 6.3×10⁻³ | 12.6 |
| 10 | 2.25×10⁻³ | 2.25 |
| 18 | 2.70×10⁻³ | 1.5 |
| 22 | 2.33×10⁻⁴ | 0.106 |
| 92 | 2.11×10⁻⁴ | 0.02293 |
| 94 | 2.16×10⁻⁴ | 0.02298 |
| 110 | 2.83×10⁻⁴ | 0.03093 |
increase of $\sigma'$ (or the decrease of $\rho$). This observation indicates that in the interval of thicknesses 10 – 20 nm we can expect a transition of the film structure from discrete islands to a continuous network [14].

4. Conclusions

In the work presented, the optical and electrical properties of thin chromium films are investigated. It is determined that thin films thinner than 10 nm possess a relatively high transmittance ($T > 65\%$). The optical constants and the complex permittivity are calculated. It is found that the imaginary part of the permittivity, $\varepsilon''$, decreases with the decrease of the films’ thickness. It is further established that the resistivity varies in the range of $6.3\times10^{-3} – 2.83\times10^{-4}\ \Omega\ cm$ and is comparable with that of ITO films.

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