# Optical investigations of CrN layers obtained by ion beam assisted deposition process+

WALDEMAR OLESZKIEWICZ<sup>1\*</sup>, EWA OLESZKIEWICZ<sup>2</sup> AND KRYSTYNA ŻUKOWSKA<sup>2</sup>

<sup>1</sup>Institute of Electron Technology, Technical University of Wrocław, Wrocław, Poland <sup>2</sup>Institute of Physics, Technical University of Wrocław, Wrocław, Poland

Chromium nitride films obtained by IBAD (Ion Beam Assisted Deposition) process were studied. Optical properties of CrN films were investigated. Refractive index and extinction coefficient of CrN layers in the spectral range of  $0.45 \div 0.65~\mu m$ . were determined by ellipsometric method. Reflectivity of these films in the spectral range of  $0.2 \div 0.8~\mu m$ . was measured by spectrophotometer SPECORD UV-VIS. The values of reflectivity and extinction coefficients of CrN films depend on the ion energy and both of them increase with the increasing ion energy.

### 1. Introduction

The dynamical ion beam assisted deposition (IBAD) technique combines the qualities of ion implantation with the PVD (Physical Vacuum Deposition) methods. In the IBAD process unbiased and negatively biased substrates were bombarded with low energy ion beam (10eV ÷ 2keV) of the great diameter (from the separated ion source) for the sputter cleaning of the substrates and during the growth of the layer as well [1, 2, 3].

The application of the low energy ion beam has a predominant advantage when the layers for microelectronics or optoelectronics and the optical coatings are deposited while the effect of the radiation damage of the substrate and the layer by ion beam is undesirable.

The ion bombardment influences the nucleation conditions and the growth kinetics (physical mixing, enhanced diffusion), as well as the final structure (morphological and crystallographic changes) and modifies the physical properties of layers [4, 5].

In the present paper, to estimate the efficiency of such activating factor as the ion bombardment, the optical investigations on CrN films obtained by IBAD proces were carried out.

Sikkens et al. [6] reported that CrN layers exhibit excellent spectral selectivity and extremely low emittance and may be applied to solar selective absorbers. These absorbers are intended for application at operating temperatures up to 200°C in high performance solar collectors.

Chromium nitride layers produced by reactive IBAD process show very good adhesion between the film and substrate, density of the film being close to the density of the bare CrN material [7, 8] and could be deposited onto substrates below 200°C.

In consequence of a good chemical stability the CrN layers are applied as anticorrosion coatings.

## 2. Experimental

Chromium nitride layers were obtained by IBAD process [9]. Nitrogen ions were generated in a Kaufman ion source designed in the Institute of

<sup>\*</sup> Corresponding author: Waldemar Oleszkiewicz, Institute of Electron Technology, Technical University of Wrocaw, Janiszewskiego 11/17, 50-372 WROCŁAW, POLAND e-mail: walole@ite.pol.wroc.pl phone: (+48-71) 320 32 59

<sup>&</sup>lt;sup>+</sup>This paper has been presented at the 6th Scientific Conference on Electron Technology ELTE-97, Krynica, May 1997.

Electron Technology of Technical University, Wrocław.

The layers were deposited onto plane parallel BK7 glass substrates, negatively biased with 100V, 300V and 500V voltage at a pressure of  $p = 4 \cdot 10^{-2}$  Pa,  $I_A = 5A$ ,  $V_A = 32V$ ,  $I_{zk} = 5A$ . The substrate current density was  $0.23\mu Acm^{-2}$  and temperature T = 327K. The examined layer thickness was  $0.15 \mu m$ .

The measurements of reflectivity were carried out by double-flux Zeiss spectrophotometer SPECORD UV VIS in the spectral range of  $0.2 \div 0.8 \,\mu m$ .

Ellipsometric measurements were made by EL6 ellipsometer in the  $0.45 \div 0.65~\mu m$  range at constant ( $\phi = 70^{\circ}$ ) angle of incidence.

Reflection ellisometry is a technique based on measurement of the polarisation states of incident and reflected waves.

The quantities measured experimentally are  $\Delta$  (the phase difference between the p- and s- components of the reflected light) and the azimuth  $\Psi$  (where tg  $\Psi$  determines the ratios of p- and s- components of the reflected light).

The functional dependence of  $\Psi$  and  $\Delta$  on the examined system parameters can be symbolically written as [10]

$$tg\Psi e^{i\Delta} = f(n_0, n, k, \lambda, \phi)$$

where:  $n_0$  - refractive index of the ambient

n – refractive index of the layer

k – extinction coefficient of the layer

 $\lambda$  – wavelength of incident light

Optical constants were determined from the formulas: [11]

an azimuth  $\Psi$  and phase difference  $\Delta$  at the constant angle of incidence.

### 3. Results and discussion

In Figs. 1 and 2 the spectral dependence of the refractive index (n) and extinction coefficient (k) for CrN samples deposited onto negatively biased substrates of  $U_p = -100V$ ,  $U_p = -300V$ ,  $U_p = -500 V$  are plotted. The bias voltage increase caused the extinction coefficient increasing what indicates better film quality (better smoothness and structure ordering).

The refractive index changes upon the bias voltage are inconsiderable.

Figs. 3 and 4 show real  $(\varepsilon_1)$  and imaginary  $(\varepsilon_2)$  part of electrical permittivity dependence on different sub-

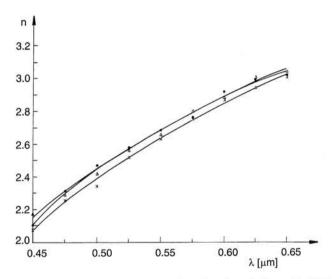


Fig. 1. Spectral dependence of refraction index of CrN layers ( $-U_p = -100V$ ,  $x - U_p = -300V$ ,  $\Delta - U_p = -500V$ ).

$$n = \left[\frac{1}{2}\left(a^2 - b^2 + n_0^2 \sin^2\phi\right) + \frac{1}{2}\sqrt{\left(a^2 - b^2 + n_0^2 \sin^2\phi\right)^2 + 4a^2b^2}\right]^{\frac{1}{2}}$$
(1)

$$k = \left[ -\frac{1}{2} \left( a^2 - b^2 + n_0^2 \sin^2 \phi \right) + \frac{1}{2} \sqrt{\left( a^2 - b^2 + n_0^2 \sin^2 \phi \right)^2 + 4a^2b^2} \right]^{\frac{1}{2}}$$
 (2)

where:

$$a = n_0 \sin\phi t g \phi \frac{\cos 2\Psi}{1 + \sin 2\Psi \cos \Delta}$$

$$b = n_0 \sin\phi t g \phi \frac{\sin 2\Psi \sin \Delta}{1 + \sin 2\Psi \cos \Delta}$$

Thus, in order to calculate the optical constants of studied layer by ellipsometry it is necessary to measure strate bias voltage values. Changes in  $\epsilon_1$  and  $\epsilon_2$  versus the bias voltage increase confirm the conclusions drawn from the extinction coefficient increasing. The dependence of reflectivity measured by spectrophotometric method on the wavelength is plotted in Fig. 5. The reflectivity value increases with the bias voltage increasing which also indicates the improvement of the film surface quality.

X-ray diffraction patterns (Fig. 6) obtained with a

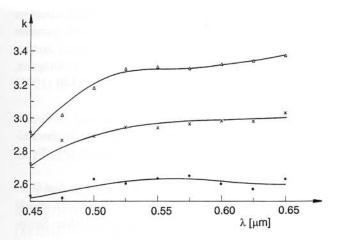


Fig. 2. Spectral dependence of extinction coefficient of CrN layers ( -  $U_p$ = -100V, x– $U_p$  = -300V,  $\Delta$  –  $U_p$  = -500V).

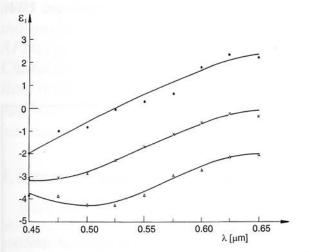


Fig. 3. Real part of electrical permittivity (1) dependence on wavelength for CrN films ( $-U_p = -100V$ ,  $x - U_p = -300V$ ,  $\Delta - U_p = -500V$ ).

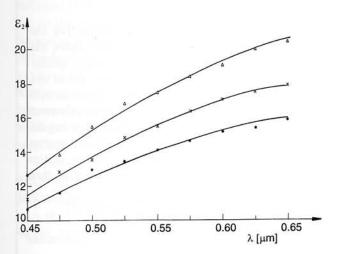


Fig. 4. Imaginary part of electrical permittivity (2) dependence on wavelength for CrN films ( $-U_p = -100V$ ,  $x - U_p = -300V$ ,  $\Delta - U_p = -500V$ ).

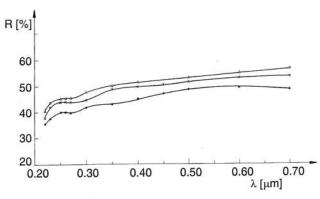


Fig. 5. Reflectivity dependence on wavelength for CrN layers deposited at the different substrate bias voltage values ( $-U_p = -100V$ ,  $x-U_p = -300V$ ,  $\Delta - U_p = -500V$ ).

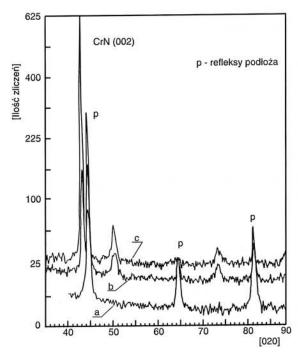


Fig. 6. X-ray diffraction patterns for CrN layers deposited onto metallic substrate (a), at  $U_p = -500V$  (b), and  $U_p = -800V$  (c) bias voltage.

HRD PHILIPS diffractometer show the diminished size of crystallites when the value of bias voltage increases which is in good agreement with the conclusions from the optical investigations.

#### References

- R.F. Bunshah: Critical Issues in Plasma-Assisted Vapor Deposition Processes, IEEE Transactions on Plasma Science 18 (1990) 846.
- 2. F.A. Smidt, G.K. Hubler: Recent advances in ion

 $Optical\ investigations\ of\ CrN\ layers...$ 

beam modification of metals, Nuclear Instruments and Methods in Physics Research **B80/81** (1993) 207.

- 3. P. Martin: *Ionization-Assisted Evaporative Processes: Techniques and Film Properties*, IEEE Transactions on Plasma Science **18** (1990) 855.
- 4. G.K. Wolf: Modification of chemical surface properties by ion beam assisted deposition, Nuclear Instruments and Methods in Physics Research **B46** (1990) 369.
- W. Ensinger: Chemical and thermodynamic influences in ion beam assisted thin film synthesis, Nuclear Instruments and Methods in Physics Research B84 (1994) 181.
- M. Sikkens, A.A.M.T. van Heereveld, E. Vogelzang: The development of high performance, low cost solar-selective absorbers, Thin Solid Films 108 (1983) 229.
- 7. A. Schröer, W. Ensinger, G.K. Wolf: A com-

- parison of the corrosion behaviour and hardness of steel samples (100Cr6) coated with titanium nitride and chromium nitride by different institutions using different deposition techniques, Materials Science and Engineering, A140 (1991) 625.
- Ch. Zili, S. Patu: Microstructure and corrosion behaviour of chromium nitride grown by dynamical ion beam mixing, Surface and Coatings Technology 51 (1992) 222.
- W. Oleszkiewicz, S. Łasisz, E. Żołnierz: Nanoszenie cienkich warstw chromu w obecności wiązki jonów (IBAD): Proc. V Ogólnopolskie Seminarium "Techniki Jonowe", 1996.
- R.M.A. Azzam, N.M. Bashara: Ellipsometry and polarized light, North-Holland Publishing Company, Amsterdam – New York – Oxford 1977.
- 11. E. Idczak: Cienkie warstwy metaliczne, PWN, Warszawa Wrocław 1974.