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Ellipsometric characterization of CrTiAlN coating deposited at low temperatures by unbalanced magnetron sputtering

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Abstract. Ellipsometric characterization is presented of a CrTiAlN hard coating deposited by unbalanced magnetron sputtering at low temperatures. Such coatings find applications where the tool material cannot withstand temperatures exceeding 200 °C. The Cr/CrN/CrTiAlN coatings deposited using the UDP-850 equipment is characterized by UV-VIS and IR ellipsometry. A FIB cross-section is made and the thickness of the coating is measured using SEM. The roughness of the coating surface is determined by AFM. The ellipsometric measurements yielded data on the phase difference Δ , amplitude ratio ψ , the frequency dependent real ($\epsilon_1(\omega)$) and imaginary ($\epsilon_2(\omega)$) part of the dielectric function and the corresponding refractive and extinction indexes $n(\omega)$ and $k(\omega)$. The optical parameters are modelled by regression analysis implemented using the WVASE© software. A very good fit is achieved between the measured optical data and the corresponding models. The results show that the ellipsometric characterization data can be used to determine the surface structure, chemical composition and optical reflection characteristics of CrTiAlN hard coatings.

1. Introduction

Surfaces produced by physical vapor deposition (PVD) have found wide industrial applications during the last decades [1]. The CrN based coatings deposited with magnetron sputtering exhibit a good corrosion resistance [2], while incorporating Al enhances their hardness [3]. Forming ternary CrTiAlN structures has resulted in a serious improvement of the tools life cycle [4]. One of the main advantages of the coatings deposited by magnetron sputtering is that the batch process takes place at low temperatures [5]. This is a very useful property for tools where increasing the treatment temperature over 200 °C decreases their hardness [6]. Such coatings continue to attract the industry interest in applications in cutting, dyeing, stamping and other tools [7]. Bearing this in mind, we deposited CrTiAlN coatings at temperatures below 200 °C by unbalanced magnetron sputtering. The optical properties of the hard coatings are affected by their chemical and physical properties [8]. Spectroscopic ellipsometry is a technique that can be used for efficient characterization of the optical properties of materials. It can provide information on the morphology, crystallinity, chemical composition, and electrical conductivity [9].

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In spectroscopic ellipsometry, the amplitude ratio ψ upon reflection of polarized light and the difference in the phase shift Δ are the basic parameters measured at different wavelengths or photon energies. These two quantities are called ellipsometric angles. In cases of materials that are either inhomogeneous or have a rough surface layer, these angles can be immediately converted to the so-called pseudodielectric function – indicated by $\varepsilon(\omega)$, which represents a fictitious model material with a homogeneous and optically thick structure. However, in order to determine the dielectric function of single layers, fitting is used to determine the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function. Of particular importance is the $\varepsilon_2(\omega)$ spectrum, since it indicates the absorption of the medium. The corresponding parameters of the dielectric function are the refractive and extinction indexes $n(\omega)$ and $k(\omega)$. Spectroscopic ellipsometry's most sophisticated feature is the construction of a theoretical model from the experimental data, which allows one to determine the dielectric function of each single layer. Fitting procedures are thereby applied for determination of the common model parameters [10]. All these features have prompted the application of ellipsometry for characterization of the optical properties of hard coatings and for in-situ control [11]. The optical properties of CrN-based coatings have been studied earlier [12], but the more complex Cr-based hard coating structures are still not well researched. The focus of this research is measuring and modeling the optical parameters of a CrTiAlN coating deposited at temperatures under 200 °C by UBMS.

2. Experiment

The experiments were performed on the UDP850/4 system for deposition of hard coatings working with a closed-field unbalanced magnetron of the Central Laboratory of Applied Physics. Singular Ti (99,99 %), Al(99,99%) and two Cr (99,99%) rectangular targets in a closed-field magnetron configuration were installed. The experimental substrates were of double-grinded high-speed steel with dimensions 13×5 mm. Prior to deposition, the substrates were ultrasonically cleaned in a special alkaline solution at 60 °C for 10 min to remove the surface contamination and then rinsed in de-ionized water. The vacuum chamber was first evacuated to 1.7×10^{-3} Pa, then Ar was introduced at a flow rate of 25 sccm. The nitrogen flow rate was controlled by a plasma optical emission monitor (OEM) with a feedback control system based on a chromium emission line; the working pressure was maintained at 0.19 Pa. When depositing a certain type of coating, a continuous direct current was applied to the corresponding target. The DC and pulse current applied to each target during coating depositions was for Cr – 5A, for Ti – 8 A and for Al – 3 A. The rotation of the sample holder was fixed at 5 rpm. In addition, a –70-V bias was applied to the substrate and the substrate temperature due to plasma heating was generally in the range of 145 – 165 °C. Before the deposition of the coating structure, the samples were cleaned with Ar plasma sputtering at a bias voltage of –500 V for 30 min. Adhesion Cr layers were first deposited for 15 minutes. An additional transition CrN layer for improving the adhesion and reducing the stress in the coating was also deposited with a gradually increasing N₂ flow. The Ti and Al targets power was lightly increased for the deposition of the CrTiAlN layer. The mechanical characteristics of the coatings (nano-hardness and adhesion) were measured with Anton Paar equipment. The nano-indentor allows loading of up to 500 mN, and the micro-indentation scratch head, a load up to 30 N. A PC system was automatically calculating the measured parameters. The UV-VIS optical characterization of the coatings was conducted by variable-angle spectroscopic (VASE) ellipsometry using ESM-300 UV-VIS (J.A. Woollam) equipment at ZONA, Johannes Kepler University, with an angle measurement range from 45 – 80° and a spectral range 190 – 1650 nm. Four reflection-geometry measurements were performed with light incident at angles of 60°, 65°, 70° and 75°. After each measurement, the equipment software calculated the optical parameters of the coating – the frequency dependent phase difference $\Delta(\omega)$, the amplitude ratio $\Psi(\omega)$, and hence the real $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ of the pseudodielectric function and the corresponding refractive and extinction indexes $n(\omega)$ and $k(\omega)$. We found that that the pseudodielectric function is almost insensitive to the angle of incidence, which in turn allowed us to assume that the pseudodielectric function is identical with the physical dielectric function. This is equivalent to the

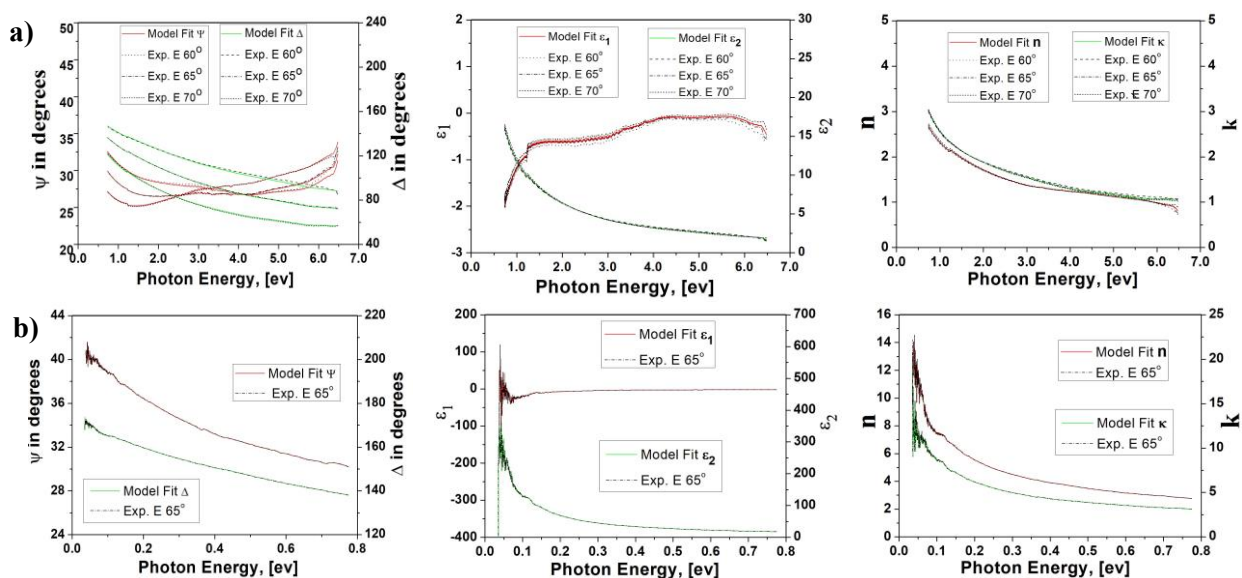
sample reflecting the light as if the rough surface layer does not contribute to the measured ellipsometric angles and, thus, pure bulk is being characterized.

The IR optical characterization was carried out using an IR-VASE (J.A. Woollam) ellipsometer with a laser emitting in the infrared spectral range $300 - 7500 \text{ cm}^{-1}$. Only one illumination angle (65°) was chosen as appropriate for the samples measured. The same optical parameters were evaluated from the equipment as with the UV-VIS ellipsometer. The complex reflection coefficients obtained were also analyzed with the regression analysis WVASE® software applying fitting algorithms [13]. The effective medium approximation (EMA) was applied to model the effect of the hard-coating surface roughness [14]. The Drude model for conductive materials, such as metals or doped semiconductors, was used to describe the free-carrier absorption [15]; the general and usual approach to fitting the dielectric function with Lorentz generalized oscillators [16], in this case for phonons, was used for the construction of the fitting model. Corroborating techniques allowed the determination of independent structural properties. The coating layer thickness set in the fitting model was measured after a focused ion beam (FIB) cross-section was made using a scanning electron microscope (SEM, Zeiss 1540 XB) with a resolution of 1 nm. The SEM software was used to define the size of the different sublayers according to their composition. The coating roughness was estimated by an atomic force microscope (AFM, Agilent Technologies).

3. Results and discussion

Different Cr/CrN/CrTiAlN coatings were deposited and the sample with the optimal mechanical parameters was chosen for UV-VIS and IR ellipsometry. The measured nano-hardness of the sample was 21 GPa. The elastic module was 366 GPa. The coating exhibited good adhesion for loads of up to 30 N.

Figure 1 presents the results for the phase difference Δ , the amplitude ratio Ψ , and the frequency dependent real and imaginary part of the dielectric function, as well as the frequency dependent refractive and extinction indexes n and k for the UV-VIS measurement (subsection a) and for the IR measurement (subsection b). In the former case, Ψ and ϵ_1 (usually called dispersion) have higher values in the low-energy region, while Δ , ϵ_2 , n and k have lower values followed by an increasing trend. In the IR results, all optical parameters are higher in the low energy region. Ψ and Δ exhibit an



almost linear decrease and, together with ε_1 , ε_2 , n and k , show normal dispersion as the photon energy increases. The decreasing trend of ε_1 indicates that the coating is with the desired compound composition, since a higher Cr metal content would lead to higher ε_1 values [17]. The refractive index n and the extinction coefficient k have values corresponding to CrN coatings, but with an opposite trend, which could be caused by a reduced number of defects [18]. A Drude response of electrons arising in the conduction band of TiN compounds could also affect n and k [19]. The measured small values of n and k are comparable to those measured by other authors for coatings deposited by magnetron sputtering [20]. The Ψ and Δ measured of our CrTiAlN coating imply semi-absorbing and absorbing properties and are similar to those of hard coatings deposited at room temperature [21].

An image taken by a SEM equipped with an FIB system is shown in figure 2 a). The different sublayers are well defined. The total thickness measured of the coating is 2.5 μm . The Cr/CrN sublayer has a thickness of 367 nm; the CrTiAlN layer has a 2.04- μm thickness. The RMS roughness of the coating surface characterized by AFM (figure 2 b) was 40.62 nm.

In the ellipsometric modeling procedure, a model material was chosen consisting of a combination of 50% “genosc” and 50% voids. The effective medium approximation layer was of a Bruggeman type with a thickness of 36.721 nm, which is near the measured roughness of 40 nm. The depolarization factor was 0.33333. The Lorentz oscillator was also defined. As is seen, the model approximates very well the results measured by both ellipsometric techniques. The small deviation kick at 1.2 eV in the UV-VIS results appears because the detector was replaced. In spite of the very good modeling results, the coating roughness could lead to depolarization, so that some slight errors might have arisen in the fitting results for n , k , ε_1 and ε_2 .

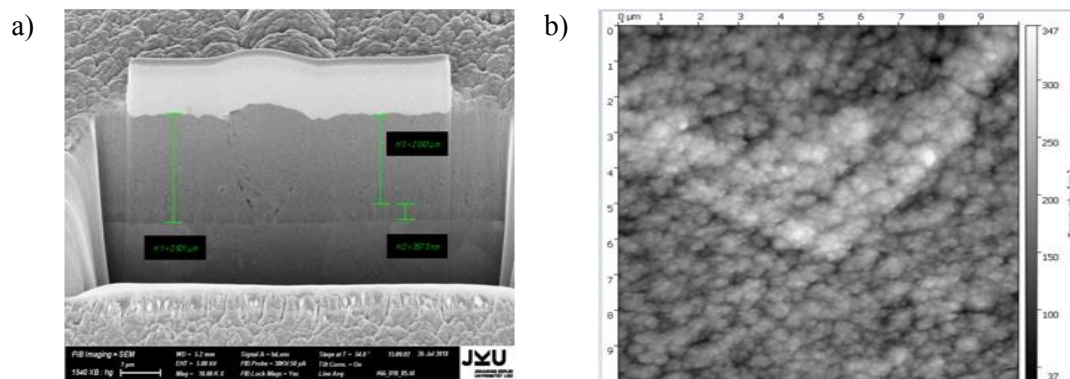


Figure 2. a) A SEM image of the FIB cut and measured coating thickness; b) An AFM image yielding an estimate of the roughness.

4. Conclusions

A CrTiAlN coating for low temperature applications was deposited by unbalanced magnetron sputtering. The optical parameters of the coating ψ , Δ , n , k , ε_1 and ε_2 were characterized by UV-VIS and IR ellipsometry. The results were processed by modeling with the WVASE© software. After cutting by FIB, AFM was used to determine the coating thickness and roughness. The fitted optical parameters correspond very well to the experimental results. The study demonstrated that the two ellipsometric techniques covering the spectral range of 50 meV – 5 eV can be used for the investigation of the physical properties of CrTiAlN coatings.

Acknowledgments

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