Determinaton of combined electrical and optical properties of titanium nitride thin films

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Abstract

For the given TiN III and TiN IV samples spectral reflectivity was measured in range from 280nm to 2000nm. The TiN thin films combined electrical and optical properties was modeled by semiclassical model which includes both intraband and interband electron transition. It is demonstrated that the semiclassical model can successfully be applied to descibe optical properties of TiN thin films, which gives the possibility to examine the optical conductivity, effective free electron concentration, screened plasma energy and related properties.

Keywords

Titanium nitride, thin films, coatings, optical properties, spectral reflectivity, semiclassical model.

Introduction

Titanium nitride, due to the exceptional mechanical properties, corrosion resistance, chemical and metallurgical stability has been proposed for various applications in semiconducter device technology [4,5] and presently is widely applied in mass production of various cutting and forming tools. Over 95% of hobs for gear cutting are now coated with TiN coatings in form of monolayer or special coating architecture.

The industrial application of TiN thin films requires a simple nondestructive method for the inspection of product quality. In past few years selective wavelength spectral range ellipsometry was found to be very good solution for characterization of TiN_x layers [6,7]. The analyses of the reflectivity spectra and color measurements of as deposited TiN coating [8,9] may be a simple visual inspection test of TiN coated components.

Theory

In oreder to calculate the optical properties of the TiN thin films from the reflectivity data, the interaction of radiation with coating material was modeled taking into account photon-free electron and photon-bound electron interactions. The model presented here will be combined screened Drude's model, which is used to describe the intraband transitions, and semiclassical model based on Lorentz theory, used to describe radiation absorption due to the interband transitions. In this model complex relative dielectric function may be described as

$$\hat{e}_r = \frac{f_0 w_p^2}{w^2 + iwG} - \sum_{j=1}^{2} \frac{f_j w_p^2}{w^2 - w_{0j}^2 + iwG_j} \qquad (1)$$

The contribution of high energy interband transitions is taken into account by introducing the background constant e_μ which is supposed to be real. The Drude (intraband) transition term contains the dumping factor G due to electron scattering inside the coating which equals to the inverse of relaxation time. This dumping factor is influenced by electron-electron and electron-phonon interactions and by the defects in material, grain boundaries, coating structure and other properties. Further on, parametar w_p is related to the unscreened plasma frequency w_{pu} by the following equation

$$w_{pu}^2 = f_0 w_p^2 \qquad (2)$$

while unscreened plasma frequency is given as

$$w_{pu} = \sqrt{\frac{ne^2}{m^* e_0}} = \sqrt{\frac{N_{eff} e^2}{me_0}} \qquad (3)$$

where n is concentration, m mass, and e charge of free electrons, while m^* is effective mass of electron, e_0 dielectric constant in vacuum, and N_{eff} effective concentration number of electrons taking part in intraband transitions.

Real and imaginary part of the relative dielectric constant can be extracted from (1), giving the result in following equation (4)

$$e_{r1} = e_{\infty} - \frac{f_0 w_p^2}{w^2 + G^2} - \sum_{j=1}^{2} \frac{f_j w_p^2 (w^2 - w_{0j}^2)}{(w^2 - w_{0j}^2) + w^2 G_j^2}$$

$$e_{r2} = \frac{f_0 w_p^2 G}{w(w^2 + G^2)} - \sum_{j=1}^{2} \frac{f_j w_p^2 G_j}{(w^2 - w_{0j}^2) + w^2 G_j^2}$$

where corresponding terms which also include dumping factors G_1 and G_2, and oscillator strengths f_1 and f_2 are called Lorentz w_{01} and Lorentz w_{02} terms.

Notice that all ten parameters in equation 1 are actual fitting parametars (e_{μ},, f_0, w_p, G, f_1, w_{01}, G_1, f_2, w_{02}, G_2). I will extract those values from the measured reflectivity of TiN-III and TiN-IV thin films and use them to get all other properties.

As it is shown in [2], when relative dielectric constant function is known, then real and imaginary part of complex refraction coefficient are given as

$$n = \sqrt{\frac{1}{2}\left(\sqrt{e_{r1}^2 + e_{r2}^2} + e_{r1}\right)} \qquad (5)$$
$$k = \sqrt{\frac{1}{2}\left(\sqrt{e_{r1}^2 + e_{r2}^2} - e_{r1}\right)}$$

In case of normal incidence of the light (the other case is too complicated) on the sample surface, the reflectance is given with the following equation

$$R = \frac{(n-1)^2 + k^2}{(n+1) + k^2} \qquad (6)$$

At this moment the model is well defined. The relative dielectric constant is related to reflectance via complex refraction coefficient. Now it is time to use this model in order to get some more information about the film. Again, as it is shown in [2], complex free electrons conductance is related to relative dielectric constant, and the relation is given with following equation

$$\tilde{s} = -iwe_0(\tilde{e}_r - 1) \qquad (7)$$

while absorption coefficient is given as

$$a = \frac{w}{c}\sqrt{2 \cdot (|\tilde{e}_r| - e_{r1})} \qquad (8)$$

The reader will easily notice that relative dielectric constant is the key to all optical and some electrical properties of TiN thin films.

Experimental

Reflectivity measurements in the UV-VIS-NIR spectral range (280nm-2000nm) were performed using Perkin-Elmer Lambda 9 spectrophotometer with an intergrating sphere in 8/d measurement geometry, including specular reflection for both TiNIII and TiNIV thin films. Photomultiplicators and Pbs detectors are used for detection of reflected beam in UV-VIS and NIR spectral range. Light sources used in experiment were deuterium lamp (for UV spectar range) and wolfram halogenous lamp (for VIS and NIR spectral range).

All measurements were made in Institute of Physics in Belgrade, Laboratory for solid state.

Results

The spectral reflectivity of the deposited TiN-III and TiN-IV thin films are given in figure 1.

The shape of the curve has all typical characteristics known from the literature [1-3, 7]: the strong absorption in the blue wavelength region with the reflectivity minimum around 430nm (for TiN-III) and 460nm (for TiN-IV), the knee at the absorption edge, and the mirror like properties in IR region.

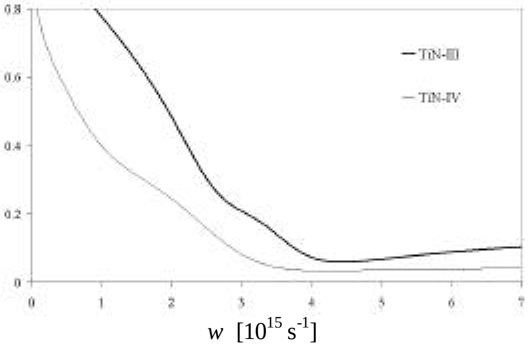

Figure 1.
Spectral reflectivity for TiN-III and TiN-IV

The fitting of experimental data was done by means of Levenberg-Marquardt gradient method using χ statistical function as the criterion. In the given spectral range the fitting was successful leading to the values of $\chi=5.0\cdot10^{-5}$ for TiN-III and $\chi=2.7\cdot10^{-6}$ for TiN-IV.

The result of fitting can now be used for evaluating all other characteristics of TiN films.

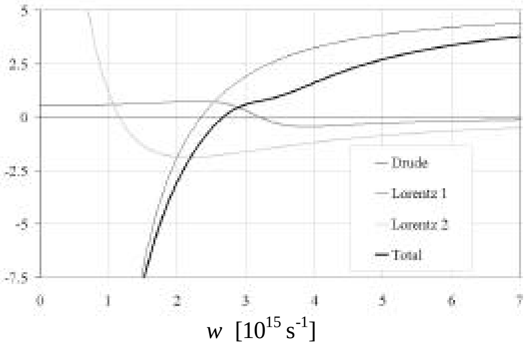

Figure 2.
Real part of the relative dielectric function for TiN-III thin films with all contributing parts

On figure 2. is presented real part of relative dielectric function with all contributing parts (Drude, Lorentz w_{01}, and Lorentz w_{02} terms) for TiN-III. From the Drude term the calculated unscreened plasma energy is 3.46eV, while the effective number of free electrons that take a part in optical processes of intrabend transition is $N_{eff}=8.68\cdot10^{21}$cm^{-3}.

Next figure shows imaginary part of relative dielectric function for TiN-III.

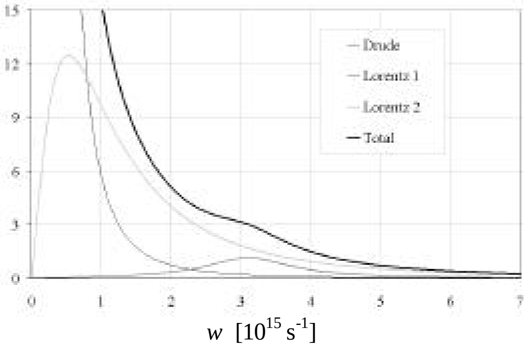

Figure 3.
Imaginary part of the relative dielectric function for TiN-III thin films with all contributing parts

There are two different frequency regions concerning the radiation-coating material interaction: for photon frequencies greater then w_{ps} and e_{r1} greater then zero, the electromagnetic wave is propagated in the thin film, while in region $w < w_{ps}$ the light is reflected. The screened plasma energy (at which $e_{r1}=0$ and $e_{r2}<<1$) is found to be $w_{ps}=5.432$eV.

Two interband transition energies are found to be at 2.103eV and 0.754eV. The Lorentz w_{02} transition is more intensive as you can see on figure 3. The corresponding broadening factors are $G_1=1.52\cdot10^{15}$s^{-1} and $G_2=2.87\cdot10^{15}$s^{-1}.

Concerning the other titanium nitride thin film – TiN-IV, unscreened plasma energy is 2.158eV and $N_{eff}=2.391\cdot10^{21}$cm^{-3}. The screened plasma energy is found to be 0.677eV.

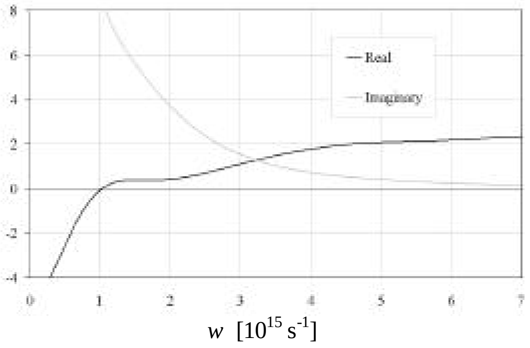

Figure 4.
Real and imaginary part of the relative dielectric function for TiN-IV thin films

Two interband transition energies are 2.103eV and 0.740eV, while broadening factors are $2.62\cdot10^{15}$s^{-1} and $2.45\cdot10^{15}$s^{-1}.

Spectral complex refraction coefficients for both TiN-III and TiN-IV films are given on figure 5.

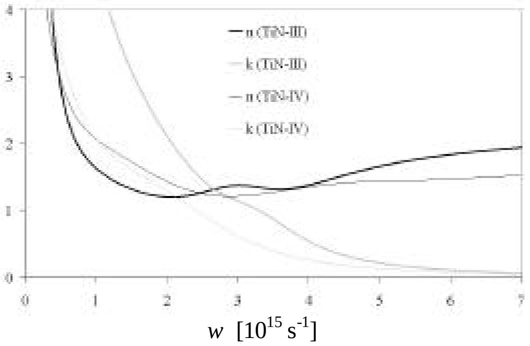

Figure 5.
Calculated values of refraction index *n* and extinction coefficient *k* for both samples

Electrical resistivity in DC mode is estimated to 88.2μΩcm for TiN-III and 975.6μΩcm for TiN-IV (extrapolation of equation (7) towards $w=0$). This result agrees well with the fact that effective number of free electrons is quite larger for the TiN-III structures.

Conclusion

It is shown that shape of the reflectivity curve can be significantly influenced by the change of the deposition parametars, with strong absorption of incident light observed in all investigated spectral regions as the common coating property.

Also, results I have presented here show very good consistence with similar results presented in [1-3,7].

At last, it has been demonstrated that semiclassical model of the incident light coating material can successfully be applied to describe optical properties of TiN thin films.

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