Effect of Defect Structure on the Optical Dispersion Properties of Thin Films of TiN_x

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Thin films of TiN_x with controlled composition were prepared by means of reactive electron-beam evaporation. Their microspecular reflectance was measured as a function of both wavelength and deviation from stoichiometry. The correlation between the electrical and optical properties as suggested by Hagen-Rubens and Drude was demonstrated.

It has been a popular notion [1–4] that both the optical dispersion characteristics and electrical properties of metals and metallic compounds can be treated on a common theoretical basis and described by the influence of an electromagnetic field on the motion of the conduction electrons, differences solely arising from the particular frequencies involved. These basic ideas have been worked out in the classical theory of Drude. Three main frequency ranges are covered by this theory:

(1) $\omega \ll 1/\tau$, where τ is a relaxation constant appearing in the equation for the electrical conductivity

$$\sigma_0 = N_\mathrm{f}\, e^2 (\tau/m) . \tag{1}$$

N_f being the number of free electrons per cm^3 and m the electronic mass. This is the normal low frequency region so that the optical conductivity σ_ω may be substituted by the electrical conductivity σ_0 for $\omega \rightarrow 0$. The metal is strongly reflecting and, as the real part of the complex dielectric constant is negligible, it can be shown [5] that the Hagen-Rubens relation is valid:

$$R \approx 1 - 2\,(\omega / 2\,\pi\,\sigma_0)^{1/2} . \tag{2}$$

(2) $1/\tau \ll \omega \ll \omega_\mathrm{p}$, i.e. the relaxation region. The reflectivity is still high, but approximately independent of wavelength. The following relation holds:

$$R \approx 1 - (1/\pi\,\sigma_0\,\tau)^{1/2} \approx 1 - 2/\omega_\mathrm{p}\,\tau . \tag{3}$$

ω_p is the oscillation frequency of the electron gas and corresponds to the plasmon edge at which the reflecting power of the metal falls to zero.

(3) $\omega_\mathrm{p} \ll \omega$. The wavelength of the incident radiation is smaller than the mean free path of the conduction electrons.

Thin films of TiN_x are characterized by an extensive defect structure, which can be controlled along with their composition. Deviations from stoichiometry have a pronounced effect on the transport properties of the compound [6]. It was pointed out by Schocken [4] that, as vacancies introduce a residual resistance in function of their number and scattering power and represent the temperature independent part of the Matthiesen rule, their influence on the optical properties in the free-electron region (near and middle IR) should be presented by such expressions as the Hagen-Rubens relation (2) and Eq. (3) in the relaxation region. As such, these equations suggest that the reflectivity should fall off as the conductivity of the samples decreases.

Thin films of TiN_x were prepared by means of reactive electron-beam evaporation. The stoichiometry of the samples could be varied in the range $0.52 < x < 1.15$ by changing the partial pressure of the nitrogen in the system. The substrate material consisted of regular soda-lime microslide glass and was kept at 300 °C during deposition. The average thickness of the films was 1500 Å.

Two infrared grating spectrophotometers were used to measure the transmittance in the spectral range from 0.83 to 2.5 μ. Values for the reflectivity were obtained with a microspecular reflectance attachment. The angle of incidence was optimized at 20° and a slight loss in intensity at the end of the optical path was corrected for by placing a variable beam attenuator in the reference beam. A highly reflective Ag-film was used to calibrate the system.

The effect of defect structure was investigated over the entire homogeneity region at a few selected values of the wavelength (1.0 and 2.0 μ). In Fig. 1, a pronounced maximum in reflectivity can be seen to coincide with a minimum in the electrical resist-

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ivity. As for the electrical conductivity [6] this maximum is not situated at the stoichiometric composition ($x=1$), indicating the large scattering power of the Ti-vacancies. It should be noted that the reflectivity R_c is a corrected value, taking into account the thickness of the samples, subtracting the transmitted radiation from the incident flux and using the following formula:

$$R_c = I_r/(1-I_t) \ . \tag{4}$$

The validity of Eqs. (2) and (3) correlating the electrical conductivity and reflectance in the near IR was checked at the selected wavelengths. By plotting $\log \varrho$ versus $\log[(1-R_c)/2]$, a straight line with slope 2 should result. This is shown clearly in Fig. 1, and the slopes are found to be 2.04 and 1.96 at 1.0 μ and 2.0 μ respectively.

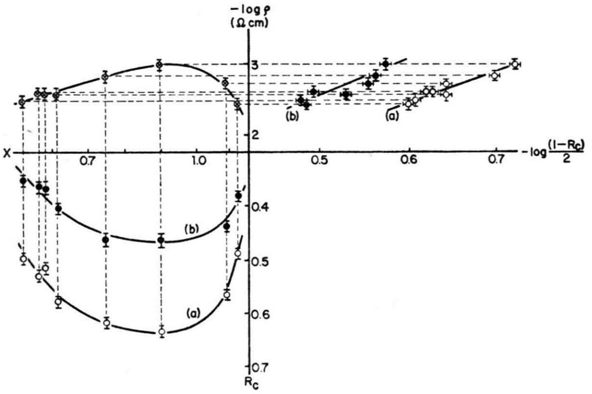

Fig. 1. Values of the corrected reflectivity R_c versus stoichiometry for TiN_x films at a) 1.0 μ and b) 2.0 μ, and correlation between the electrical resistivity and reflective power.

The variation in optical reflectance as a function of wavelength was studied for two films of different composition, chosen specifically because they are situated at the upper and lower limits of the conductivity range (Figure 2). Close to stoichiometry ($TiN_{0.90}$), the microspecular reflectance remains constant down to a specific wavelength (≈ 1.6) which corresponds to the onset of the transition region associated with the plasmon edge. Because of the defective nature of the films, this transition is not sharp and smeared out over a broad spectral range over which the specific absorption frequencies of the bound electrons overlap the uniform background of the free electrons. The transition region can be seen to extent into the visible spectrum, indicating that free electron dispersion still plays a role in the optical behavior of the compound in part of the visible range.

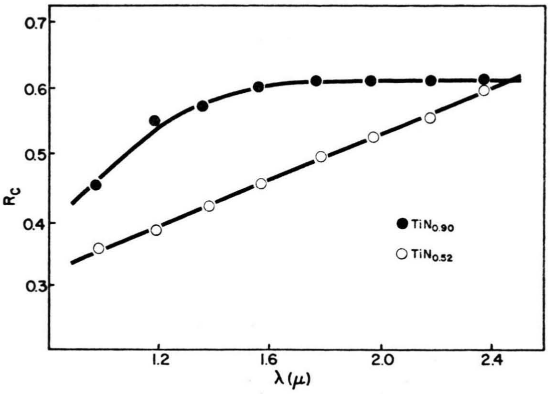

Fig. 2. Variation in corrected reflectivity with wavelength for a few selected TiN_x-films of different compositions.

The onset of this plasmon edge should shift towards smaller wavelengths for more defective samples, corresponding to a decrease in mobility and consequent increase in oscillation frequency of the collectivized electrons. This could not be observed however for $TiN_{0.52}$. The reflectance is seen to vary linearly with wavelength, but is not constant.

A tentative explanation might be the increased influence from the bonding electrons on the optical properties of the more defective sample. This is in complete agreement with the expermental observation that the number of collectivized electrons decreases with deviation from stoichiometry [6]. As more atoms find themselves in surroundings deviating from the normal crystal structure, their resonance frequencies will be slightly shifted from the normal position. A superposition of these shifted frequencies gives rise to the observed flattening of the spectral features. Furthermore, the distortion energies introduced by the vacancies are no longer small as compared to the bonding energies and interactions between the scattering potentials set up by the vacancies become more probable.

Another, more plausible explanation may be that whereas for $TiN_{0.90}$ the plasmon edge and relaxation part of the free electron region were detected, the curve obtained for $TiN_{0.52}$ corresponds to the actual frequency range in which the Hagen-Rubens relation is valid (as proven in Figure 1). The relaxation part may be considerably shorter than in the previous sample and the plasmon edge simply doesn't show as it is shifted completely into the visible spectrum. Strong evidence for this premise was found in the literature on bulk TiN_x[2]. This would also explain the observation that actually the reflectance of the more defective sample becomes larger than that for $TiN_{0.90}$ at longer wavelengths, as the samples are situated in completely different regimes of the Drude theory.

Acknowledgements

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