JOURNAL OF MATERIALS SCIENCE 26 (1991) 5843–5847

Optical properties of vanadium thin films

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The optical constants of vanadium thin films of different thicknesses were determined in the spectral range of 2.5 to 8.5 μm. These optical constants were used to evaluate some microcharacteristics of vanadium thin films such as the free charge concentration, the relaxation time, the static conductivity, the electron velocity at the Fermi surface, the mean free path and the specularity parameter.

The determination of the microcharacteristics were carried out in conjunction with Drude's theory of free charge carriers as well as with anomalous skin effect theory.

1. Introduction

Investigations of the optical properties of thin metal films are of great importance in studies of the properties of solids. The optical constants in conjunction with either Drude's theory or the anomalous skin effect can be used as a sensitive tool in the determination of some microcharacteristics of metals and semimetals.

The aim of this work is to determine the optical constants of vanadium thin films in the spectral range of 2.5 to 8.5 μm. The obtained optical constants of vanadium thin films were used in conjunction with both Drude's theory of free carriers and anomalous skin effect theory to calculate the following microcharacteristics

(i) the free charge concentration n_c.
(ii) the relaxation time τ.
(iii) the static conductivity σ.
(iv) the electron velocity at Fermi surface v_f and
(v) the specularity parameter P.

2. Experimental procedure and results

In order to determine the optical constants n and k of polycrystalline vanadium thin films in the spectral range of 2.5 to 8.5 μm, some samples of different thicknesses (50 to 100 nm) were prepared in vacuum of 10^{-5} Torr by thermal evaporation on mica discs held at room temperature during the deposition process. The deposition rate was kept constant at $3\,\mathrm{nm\,s^{-1}}$. Transmittance measurements for each sample were carried out at normal incidence using PYE UNICAM SP-300 Infrared Spectrophotometer.

Fig. 1 illustrates the transmittance T as a function of wavenumber for four samples, as a representative example. Curves a, b, c and d correspond to the thicknesses 50, 57, 80 and 100 nm, respectively.

2.1. The optical constants of V thin films

Generally, the determination of optical constants (n and k) requires at least two physical measurable quantities which may be the transmittance (T) and the reflectance (R). For high absorbing thin metallic films, however, transmittance at normal incidence of some samples of different thicknesses can be used to determine the absorption index k using the following relation [1]

$$k = \frac{\lambda}{4\pi}\frac{\ln(1/T_2) - \ln(1/T_1)}{t_2 - t_1} \tag{1}$$

where λ is the wavelength at which the transmittance T_2 and T_1 were measured for two samples of thicknesses t_2 and t_1, respectively. Therefore, knowing the transmittance T_1 and T_2 at certain λ for two successive samples of known thicknesses t_1 and t_2, the absorption index k can be determined. The same procedure can be repeated for the whole spectrum under test.

The refractive index n for such samples can be determined using

$$T = \frac{16n_1n_2(n^2 + k^2)}{[(n_1 + n)^2 + k^2][(n_2 + n)^2 + k^2]} \times \exp\left(\frac{-4\pi tk}{\lambda}\right) \tag{2}$$

where, n_1 and n_2 are the refractive indices of air and substrate, respectively. The obtained values of both n and k determined in the infrared region, are illustrated in Fig. 2.

2.2. Optical constants of V thin films in conjunction with Drude's theory of free carriers

According to Drude's theory [2], there are two relations relating the optical constants (n and k) to the wavenumber of the incident radiation ($\bar{\nu}$). These two relations are

$$(k^2 - n^2 + 1)^{-1} = (\bar{\nu}_o)^{-2}[(\bar{\nu})^2 + (\bar{\nu}_R)^2] \tag{3}$$

$$(2nk\nu) = (\bar{\nu}_o)^{-2}(\bar{\nu}_R)^{-1}[(\bar{\nu})^{-2} + (\bar{\nu}_R)^{-2}] \tag{4}$$

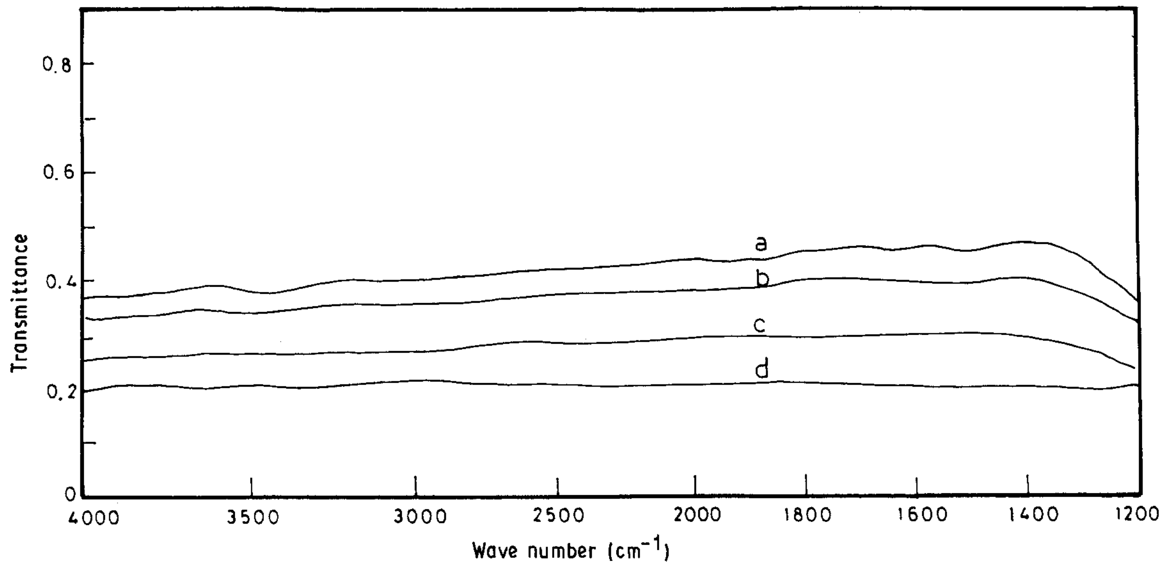

Figure 1 Relation between transmittance and wavenumber for four samples of different thickness. (a 50 nm, b 57 nm, c 80 nm, d 100 nm)

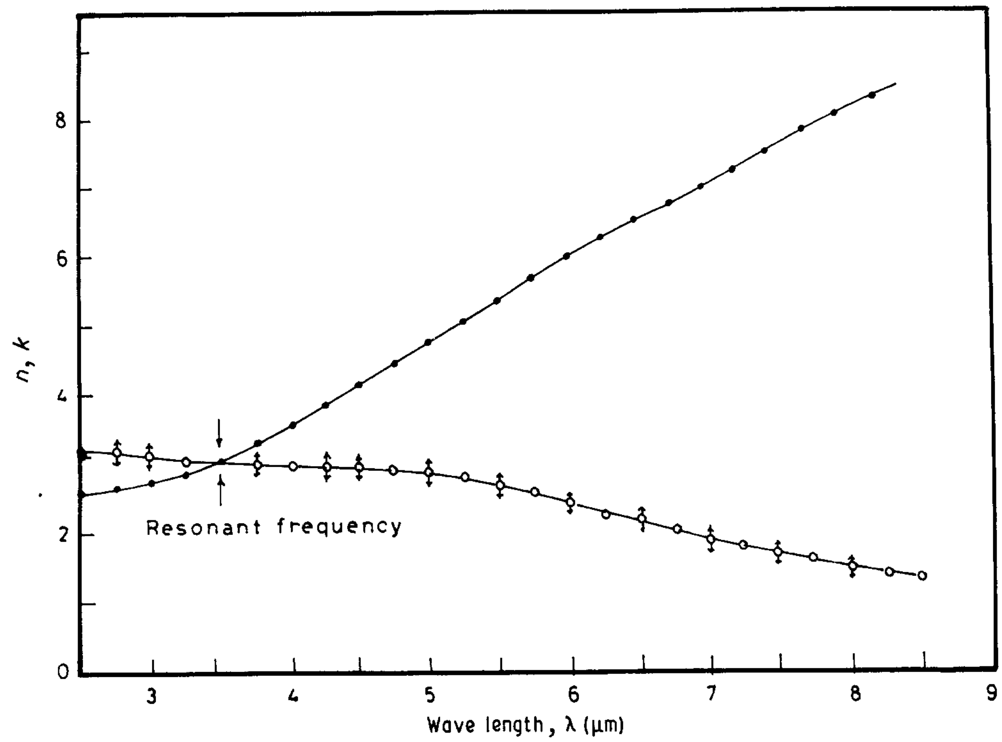

Figure 2 Relation between n (○) and k (●) against λ for thin V films.

where

$$(\bar{\nu}_o)^2 = n_c e^2/\pi m^* c^2 \tag{5}$$

and

$$\bar{\nu}_R = 1/2\pi c\tau \tag{6}$$

where n_c is the number of conduction electrons per unit volume, e the electron charge, τ the relaxation time, m^* the effective mass and c light velocity in vacuum.

From a plot of $(k^2 - n^2 + 1)$ as a function of $(\bar{\nu})^2$ as shown in Fig. 3 one can, therefore, get a linear relation, the slope of which is $= 1/(\bar{\nu}_o)^2$. $(2nk\bar{\nu})^{-1}$ is also plotted against $(\nu)^{-2}$ as illustrated in Fig. 4. The slope of the new straight line representing the second relation equals $1/(\bar{\nu}_o)^2(\bar{\nu}_R)$. Accordingly, using the two slopes together, $(\bar{\nu}_o)^2$ and $(\bar{\nu}_R)$ can be determined. The obtained values for $(\bar{\nu}_o)^2$ and $(\bar{\nu}_R)$ are $108\ \mathrm{cm}^{-2}$ and $44.5 \times 10^{-5}\ \mathrm{cm}^{-1}$, respectively.

Using these values in conjunction with Equations 5 and 6, the number of conduction electrons per unit volume $n_c = 11.16 \times 10^{20}\ \mathrm{cm}^{-3}$ taking into account that $m^* = m = 9.1 \times 10^{-28}$ g, and the relaxation time $\tau = 11.9 \times 10^{-15}$ s.

If the number of conduction electrons per unit volume (n_c) and the relaxation time (τ) are known, the static conductivity (σ) in vanadium films can be calculated using

$$\sigma = n_c e^2 \tau/m^* \tag{7}$$

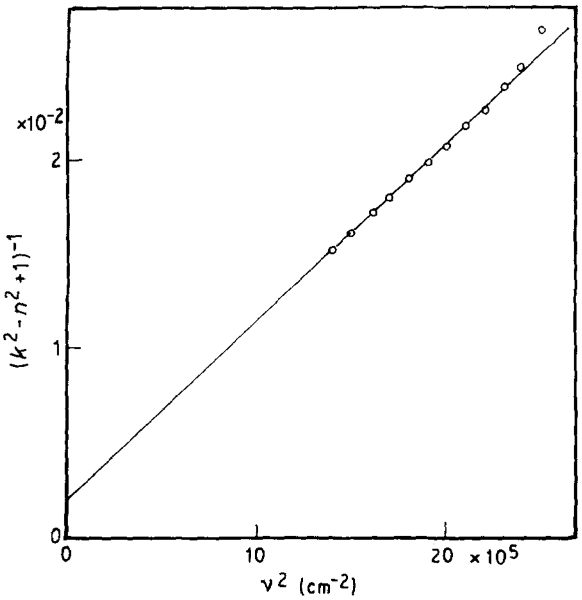

Figure 3 Relation between $(k^2 - n^2 + 1)^{-1}$ and (ν^2) for thin vanadium films. Slope $= 0.1 \times 10^{-7}$, $\nu_o^{-2} = 10^{-8}$ cm^2, $\nu_R = 0.447 \times 10^3$ cm^{-1}.

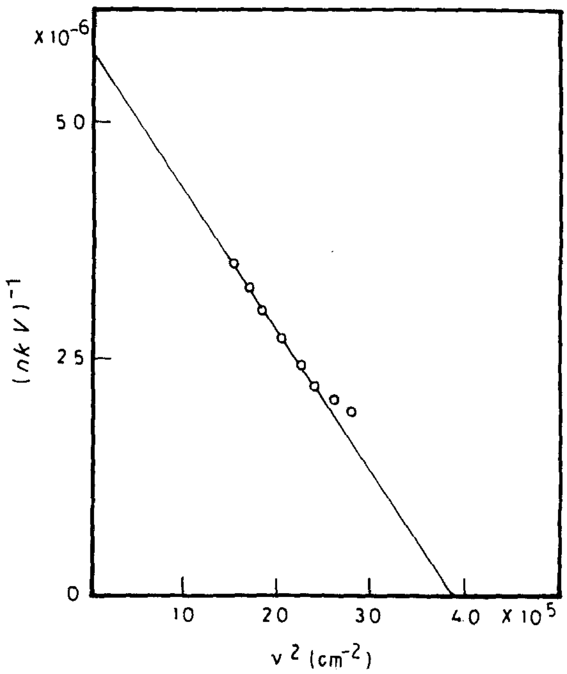

Figure 4 Relation between $(2\,nk\nu)^{-1}$ and (ν^2) for thin vanadium films. Slope $= 1.513 \times 10^{-11}$, $\nu_R = 0.66 \times 10^{-3}$ cm^{-1}.

On the other hand, the static conductivity σ can be determined directly using the values of $(\bar{\nu}_o)^2$ and $(\bar{\nu}_R)$ as

$$\sigma = c(\bar{\nu}_o)^2/2(\bar{\nu}_R) \tag{8}$$

It was found that $\sigma = 3.355 \times 10^{15}$ (e.s.u.).

The electron velocity at the Fermi surface V_F can be determined using one of the two following equations

$$V_F = \left(\frac{3(\bar{\nu}_o)^2 h^3 c^2}{8m^* e^2}\right)^{1/3} \tag{9}$$

or

$$V_F = (3n_c h^3/8m^{*2}e^2)^{1/3} \tag{10}$$

If $(\bar{\nu}_o)^2$ or n_c, the Planck constant h and the effective mass of the electron m^*, are known, it was found, therefore, that

$$V_F = 3.72 \times 10^7 \text{ cm s}^{-1}.$$

2.3. Optical constants of Vanadium thin films in conjunction with the anomalous skin effect

We shall now consider the optical constants (n and k) of vanadium thin films in conjunction with both measurements of the electrical conductivity as well as in conjunction with the theory of the anomalous skin effect to determine the number of conduction electrons per unit volume, (n_c) the relaxation time (τ), and the product of $V_f(1 - P)$ where P is the specularity parameter and V_f the electron velocity at the Fermi surface.

The dispersion relations obtained by Dingle [3] for the optical constants of metals in the infrared region according to the first approximation are

$$\varepsilon = n^2 - k^2 = -\frac{\lambda^2}{c^2}\frac{\sigma}{\pi\tau} \tag{11}$$

$$nk = B\frac{\lambda^3}{c^3}\frac{\sigma}{4\pi^2\tau^2} \tag{12}$$

and

$$B = 1 + \frac{3}{4}(1 - P)\frac{l}{c}\left(\frac{\pi\sigma}{\tau}\right)^{1/2} \tag{13}$$

The expression for ε is identical to the analogous formula given by the classical Drude–Zener theory for the case $|\varepsilon| = |n^2 - k^2| \gg 1$. The latter inequality is practically satisfied for many metals in the infrared region of the spectra. This agreement is due to the fact that in the Drude–Zener theory the quantity $\varepsilon = n^2 - k^2$ is independent of the mean free path of electrons in the metals, but depends only on the wavelength and the concentration of conduction electrons. This means that the formula for ε is invariant with respect to the nature of the skin effect.

From the measured values of n and k, it may, therefore, be looked upon as one of the main problems in metal optics since the formula for ε has a clear classical meaning and is independent of the particular mode employed [4].

A second approximation, Dingle' dispersion relations, may be written in the form

$$\frac{k^2 - n^2}{\lambda^2} = A - B\lambda^2 \tag{14}$$

$$\frac{nk}{\lambda^3} = G - D\lambda^2 \tag{15}$$

where

$$A = \frac{\sigma}{\pi c^2 \tau^2},\quad G = \frac{1}{c^3}\frac{\sigma}{4\pi^2\tau^2} \times\left[1 + \frac{3}{4}(1 - P)\frac{l}{c}\left(\frac{\pi\sigma}{\tau}\right)^{1/2}\right] \tag{16}$$

The dependence of $(k^2 - n^2)/\lambda^2$ and (nk/λ^3) on λ^2 should be linear, with intercepts yielding A and G, respectively. The magnitude of A determined in this way may be used in conjunction with the expression for the static conductivity $\sigma = n_c e^2 \tau / m^*$ to calculate the number of conduction electrons per unit volume, provided the effective electron mass m^* is known,

$$n_c = \frac{\pi c^2 m^* A}{e^2} \tag{17}$$

If the static conductivity σ and the intercept A are known, it is also possible to determine the relaxation time from

$$\tau = \frac{\sigma}{\pi c^2 A} \tag{18}$$

Finally the intercept G can be used to determine the product of $(1 - P)l$ where P is the specularity parameter and l the mean free path

$$(1 - P)l = \frac{4}{3\pi A^{1/2}}\left(\frac{4\sigma G}{cA^2} - 1\right) \tag{19}$$

Dividing (19) by (18) we then obtain $(1 - P)V_F$ where $V_F = l/\tau$ is the Fermi velocity of an electron. Separate determination of P and V_F by optical means alone is impossible.

Fig. 5 represents simultaneously the two relations

$$\frac{k^2 - n^2}{\lambda^2} = f(\lambda^2) \quad \text{and} \quad \frac{nk}{\lambda^3} = g(\lambda^2).$$

as indicated by the curves 1 and 2, respectively.

The observed intercepts A and G are equal to 1.07 $\times 10^8$ cm^{-2} and 0.27×10^{11} cm^3, respectively.

Using these two values in conjunction with the bulk electrical conductivity measurements, carried out before at room temperature for vanadium films deposited onto glass substrates [5], the number of conduction electrons (n_c), the relaxation time (τ), the product $(1 - P)l$ and the product $(1 - P)V_F$ can be evaluated using Equations 17 to 19, respectively.

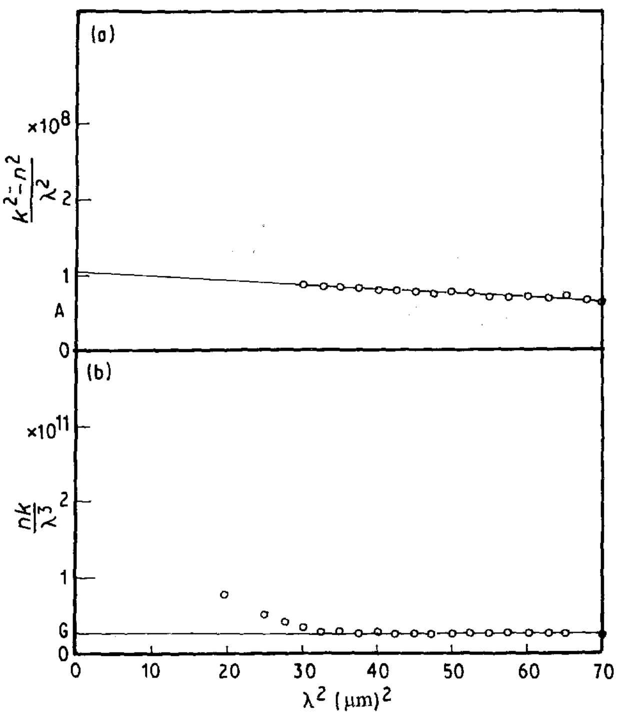

Figure 5 Relation between (a) $(k^2 - n^2)/\lambda^2$ ($A = 1.07 \times 10^8$ cm^{-2}) and (b) nk/λ^3 ($G = 0.27 \times 10^{11}$ cm^{-3}) with λ^2 (μm)^2 for thin V films.

TABLE I Values of n_c, τ, $(1 - P)l$ and $(1 - P)V_F$ for V films

n_c (cm^{-3})	τ (s)	$(1 - P)l$ (nm)	$(1 - F)V_F$ (cm s^{-1})
11.94×10^{20}	11.9×10^{-15}	40.8	2.53×10^8

TABLE II

	σ (e.s.u.)	n_c (cm^{-3})	τ (s)
Electrical	3.474×10^{15}	—	—
Drude	3.355×10^{15}	11.16×10^2	11.9×10^{-15}
Skin effect	3.353×10^{15}	11.94×10^{20}	11.09×10^{-15}

Returning to the values of ρ_o for vanadium films measured at room temperature [5]. The obtained values are given in Table I.

Returning to the dark electrical resistivity determined for vanadium film of infinite thickness ($\approx$ bulk resistivity ρ_β), the mean free path of the conduction electrons l can be determined using

$$l = (3\pi^2)^{1/3} \hbar / e^2 n^{2/3} \rho_o \tag{20}$$

It was found that l has a value of 57.3 nm using this value in conjunction with the obtained values of $(1 - P)l$, $(1 - P)V_F$ and τ, the specularity parameter P as well as the Fermi velocity of the conduction electrons at the Fermi surface can be determined. The obtained values are

$$P = 0.288 \quad \text{and} \quad V_F = 4.81 \times 10^8 \text{ cm s}^{-1}.$$

The obtained results for n_c, τ, l, P and V_F are in good agreement with the corresponding data given before, using Drude's theory as they have approximately the same order.

Table II indicates the results obtained representing σ, n_c and τ calculated using the optical properties in comparison with results calculated using electrical measurements.

3. Discussion

The case when the specularity parameter $P = 1$ corresponds to specular reflection, while the case when $P = 0$ corresponds to diffuse reflection. In reality, there is an intermediate value of specularity parameter P. Separate determination of the specularity parameter P using the optical constants alone is impossible, therefore using the obtained values of $(1 - P)l$ determined from the graphical treatment of Dingle's relations in conjunction with the dark electrical resistivity ρ_o of vanadium thin films of infinite thickness determined using F–S representation, the specularity parameter was found to be 0.288. Along with the optical constants of vanadium thin films, the micro-characteristics i.e., n_c, τ, σ, v_f and l can be determined.

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Received 30 July 1990
and accepted 15 January 1991