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Structure and optical properties of thin titanium films deposited on different substrates

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Thin films of titanium were deposited on different substrates at room temperature. Measurements were made of the optical constants and of the transmittance of titanium films evaporated on to fused quartz. Films of titanium 10 to 40 nm thick were found to have quite uniform transmittance throughout the visible spectrum. Because titanium getters strongly during its evaporation, pure and compact titanium films can only be produced by fast evaporation under extremely good vacuum conditions. All films prepared for optical measurements, for X-ray and for scanning electron microscopy studies were, therefore, deposited at a pressure $\sim 10^{-4}$ Pa and with deposition rate $\sim 4\,\mathrm{nm\,sec^{-1}}$. The measurements were made using a Beckman double-beam spectrophotometer UV 5230, Siemens D 500 X-ray diffractometer, and SEMCO nanolab 7 scanning electron microscopy.

1. Introduction

In recent years, titanium has gained increasing importance as a structural material, and extensive information on most of its physical and chemical properties has been reported in the literature [2]. Recent advances in the evaporation technique have made it easier to prepare good titanium films with surfaces more defined than those of polished bulk metal [3]. It is the purpose of this paper to present data on optical constants of titanium in the visible region and to discuss the optical properties of semitransparent films besides studies for X-ray and scanning electron microscopy.

The optical constants n and k were determined for some transition metals from reflection and transmission measurements on vacuum-evaporated polycrystalline thin films at room temperature, in the spectral range 0.5 to 6.5 eV. Transmission measurements were made on films in the thickness range 20 to 50 nm. Many transition metals oxidize rapidly in air and a detailed analysis of the effect of oxidation on the measured quantities indicates that it is small [4].

Reflectance of thermally oxidized mechanically polished titanium surfaces was measured with a spectrometer at 588.9 to 589.9 nm. These measurements provided a method for determining the optical constants of the metal and the thermal oxide. The complex optical constant calculated was found to be $\tilde{n} = 2.33 - 3.18i$ where i is the imaginary part [5]. This result can be contrasted with that of Bradford and Hass [3] who measured the optical constants of opaque evaporated titanium films at several wavelengths. From linear interpolations of their data, an optical constant of $\tilde{n} = 2.72$ to $3.48i$ would be obtained for an evaporated titanium film at $\lambda = 589.2$ nm [5]. The oxide films growing on titanium are weakly absorbing in the visible light region [6, 7].

The reflectivity and transmissivity of titanium films were measured [8] in the range 160 to 45 nm in order to compare the frequency at which the films change from a reflecting to a transmitting medium with the plasma frequency predicted by Pines [9, 10] and also with electron energy characteristic losses in metals observed by Marton *et al.* [11] and by Powell [12]. The optical transmissivity of thin films and their electron characteristic energy absorption values are each interpretable in terms of the frequency dependence of the complex dielectric constant [13].

Energy loss spectra in the first transition metals have been performed by transmission of 35 eV electrons through thin films (20 to 40 nm) in the spectral range 2 to 120 eV. Experimental data processing enables one to distinguish between signal scattering volume losses and surface losses. Characteristic functions, such as the energy loss function, the complex dielectric constant, and the optical absorption coefficient are computed and compared with results obtained by different methods [14, 15].

Optical constants of electrolytically polished titanium were determined in the spectral range $\lambda = 0.4$ to $10\,\mu$m. The following characteristics were also determined: the conduction electron density $N = 0.63 \times 10^{22}\,\mathrm{cm^{-3}}$, the effective frequency of collisions between the conduction electrons $V = 1.9 \times 10^{14}\,\mathrm{sec^{-1}}$, and the electron–phonon interaction constant, $\lambda_{\mathrm{eph}} = 0.34$ [16, 17].

Thin titanium films are deposited on glass substrates maintained at various elevated temperatures. X-ray studies show that higher substrate temperatures cause growth of the $\{10\bar{1}1\}$ orientation in preference to the $\{0002\}$ orientation and also increase the grain size in the films [18]. X-ray reflectivity across cobalt and titanium $L_{2,3}$ absorption edges was measured as a function of energy by means of continuous radiation from a tungsten anode in a grating spectrometer. The real and imaginary parts of the refractive index were obtained from the absorption curves and an exact Kramers–Kronig analysis. The X-ray intensity was

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calculated as a function of energy by means of the Fresnel formula [19].

2. Preparation of titanium films

Titanium (99.999%) was evaporated *in situ* from a tungsten boat. The titanium-vapour source was located about 10 cm from the substrate (fused quartz, freshly cleaved mica and rocksalt), and a shutter which was mounted close to the substrate was closed. After a constant evaporation speed was obtained, the shutter was opened to allow film deposition and closed when the coating reached the desired thickness. Film thickness was measured using a Tolanskey interferometer [20]. For scanning electron microscope observations, the film and mica or rocksalt substrate were mounted on a standard specimen stub and examined in an SEMCO nanolab 7 scanning electron microscope operating at 15 kV. A thin coating (≈ 10 nm) of gold was deposited on to the metal film and substrate attached to the stub, prior to examination in the scanning electron microscope, to enhance the conductivity and secondary electron emission characteristics of the overgrowth.

3. Results and discussion

3.1. X-ray diffraction data and scanning electron microscopy for thin titanium films

The analysis of the structure of titanium films evaporated on to crystalline substrates (freshly cleaved mica and rocksalt) was carried out using an X-ray diffraction technique and scanning electron microscopy in order to clarify the characteristic features of the phases and the structure of the deposited layers.

The X-ray diffractograms (b, c) shown in Fig. 1 are of freshly deposited titanium films compared to the powder pattern (a). The analyses of the thin film pattern are presented in Table I compared to the ASTM card file data. The difference between some of the values from the ASTM data is probably due to

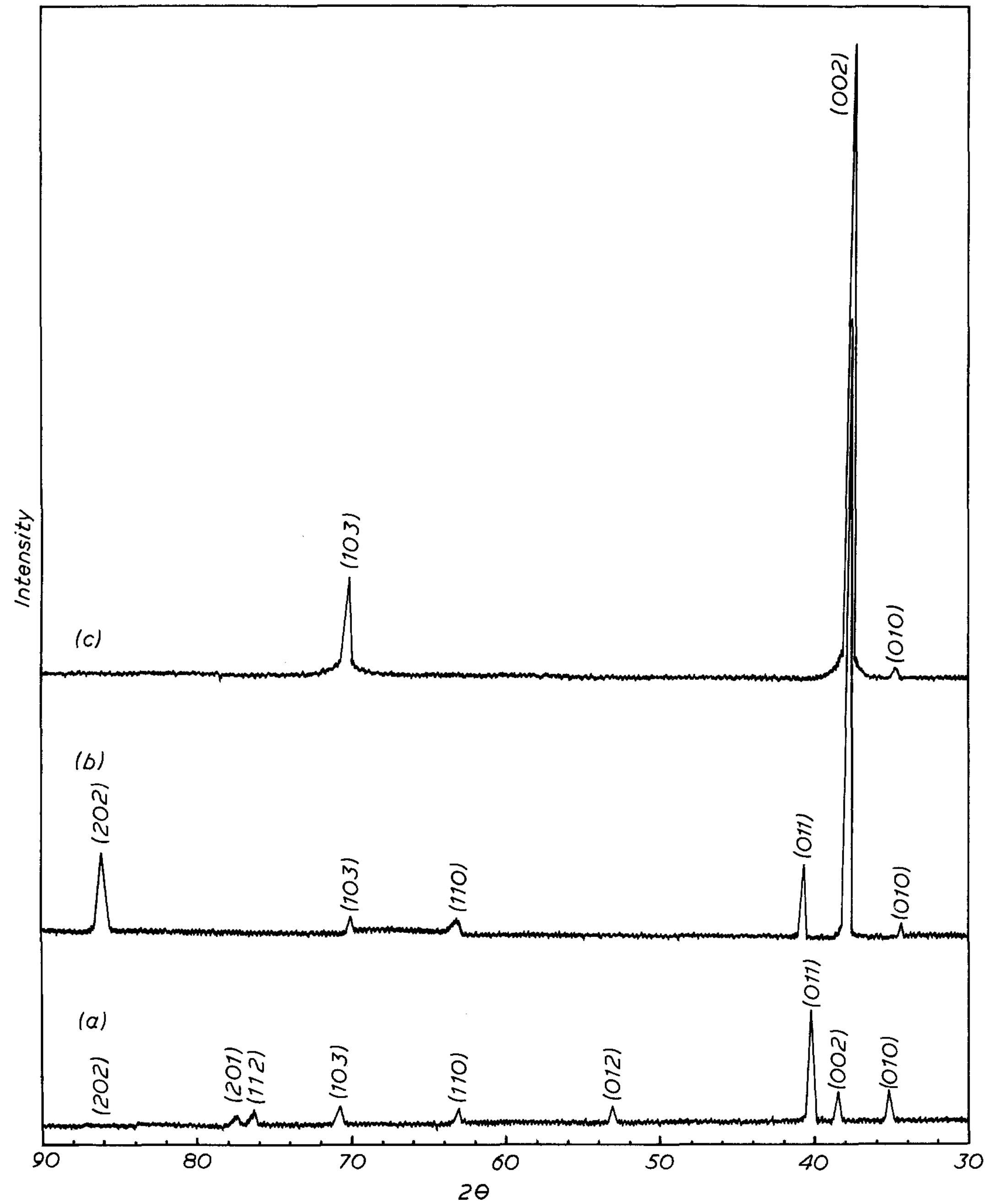

Figure 1 X-ray diffraction pattern for 130 nm film deposited on to cleaved mica (b) and rocksalt (c) substrates compared to the powder pattern (a).

TABLE I X-ray diffraction data of titanium powder and films deposited on mica and NaCl

Substrate	$d_{\text{calc.}}$	$(I/I_0)_{\text{calc}}$ (%)	$d_{\text{X-ray}}$	*hkl*	$(I/I_0)_{\text{X-ray}}$ (%)
Powder	2.5544	29.7	2.557	010	30
	2.3363	27	2.342	002	20
	2.242	100	2.244	011	100
	1.7262	16.2	1.726	012	19
	1.4742	13.5	1.475	110	17
	1.3346	16.2	1.332	103	16
	1.2442	16.2	1.247	112	16
	1.2316	11	1.233	201	13
	1.1215	3	1.122	202	2
Mica	2.6048	4	2.557	010	30
	2.3659	100	2.342	002	20
	2.2201	14	2.244	011	100
	1.4721	4	1.475	110	17
	1.3412	5	1.332	103	16
	1.1252	13	1.122	202	2
NaCl	2.5615	3	2.557	010	30
	2.3659	100	2.342	002	20
	1.3346	16	1.332	103	16

in-plane tensile stresses that produce normal compression according to Poisson's ratio. Tensile stresses in the plane of the film arise from film–substrate interactions [21]. The analysis indicated that films deposited on rock salt show a predominant orientation; however, films deposited on mica are randomly oriented.

Figs. 2a and b show scanning electron micrographs of a typical film of freshly evaporated titanium deposited on to mica and rock salt substrates, respectively. It is evident that most particles have sharp geometrical shapes of the possible projections of the hexagonal crystals on a plane. In the case of mica and rocksalt as a substrate, deposition will be governed by the relation between the interatomic spacing of the network of both the substrate and titanium, and by the substrate surface features. Hence, the deposition will mainly occur at certain preferred sites. In general, rocksalt crystals were found to contain edge and screw dislocations in addition to steps [22] which act as preferred sites for crystal growth. Meanwhile, mica was found to contain steps, defects planes inclined to the surface and dislocation lines ending at its cleavage plane [23].

3.2. Optical properties of titanium films

At any wavelength, the optical behaviour of a metal may be described by its complex optical constant $\tilde{n} = n - ik$, where n is the refractive index and k is the absorption coefficient. The optical transmission methods used for the determination of this constant are greatly affected by the state of the metal surface. The theory and various applications of the method have been discussed extensively in the literature [24]. It was found that the optical constants of materials in the form of thin films are usually a little, and often greatly, different from those of the material in bulk.

Fig. 3 shows the transmittance of various titanium films in the visible range from 300 to 800 nm. The transmissivity curve represents data taken on a film 25, 30 or 40 nm thick, evaporated in the external chamber and transferred immediately to the experimental chamber within the monochrometer. When this procedure was followed transmission values did not change for any metal films over at least a two hour period [4]. Films in this thickness range have quite uniform transmittance throughout the visible spectrum. These films, however, are only neutral in the visible region [3]. For comparison, transmittance has

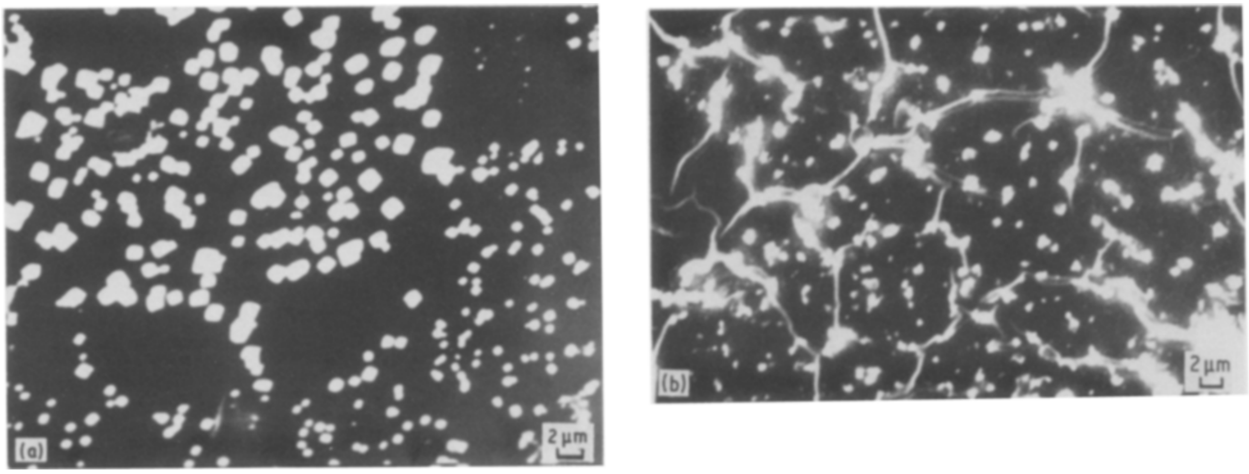

Figure 2 Scanning electron micrographs of a freshly deposited titanium film on mica and rocksalt substrates (t = 130 nm).

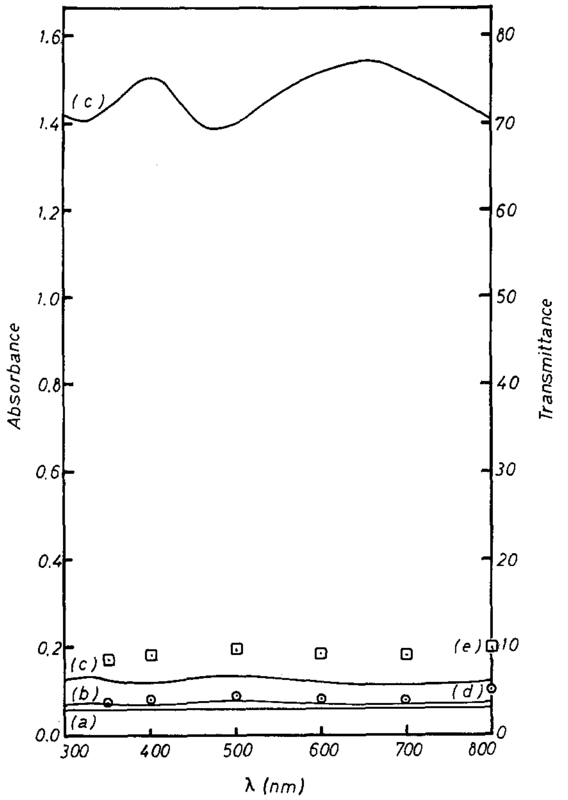

Figure 3 Spectral dependence of the transmission of titanium films in the visible range. (a) $t = 40\,\text{mm}$, (b) $t = 30\,\text{nm}$, (c) $t = 25\,\text{nm}$, (d) $t = 33\,\text{nm}$ (from [3]), (e) $t = 23\,\text{nm}$ (from [3]).

been plotted together with the results of Hass and Bradford [3] taken at 300 K. The transmittance in Fig. 3 increases very slowly as the wavelength increases; however, the transmittance decreases with increasing film thickness. The spectral variation of absorbance, $\log_{10}$ (1/transmittance), for a thin film of titanium about 25 nm thick, is shown in the same figure. The absorbance is measured from an arbitrary zero at 2.0 eV. The curve exhibits absorbance maxima at 400 and 650 nm and an absorbance at 480 nm.

The properties of thin metal films deposited on a substrate of index n_1 are examined by measuring the transmission of these films. These properties are expressed by the index of refraction (n) and the absorption coefficient (k) which are related to the transmission by the following equations [25, 26]

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

$$T = \frac{16\,n_1\,(n^2 + k^2)}{[(n+1)^2 + k^2]\,[(n_1 + n)^2 + k^2]} \times \exp(-4\pi k t/\lambda) \qquad (2)$$

Theoretical calculations are usually expressed in terms of the complex dielectric constant $\varepsilon_1 + i\varepsilon_2$, where

$$\varepsilon_1 = n^2 - k^2,$$
$$\varepsilon_2 = 2nk \qquad (3)$$

for graphical presentation of the results on the transition metals [4], the conductivity $\sigma_1 + i\sigma_2$ is more convenient than the dielectric constant, they are related by

$$\sigma_1 = \varepsilon_2\,\omega/4\pi,$$
$$-\sigma_2 = (\varepsilon_1 - 1)\,\omega/4\pi \qquad (4)$$

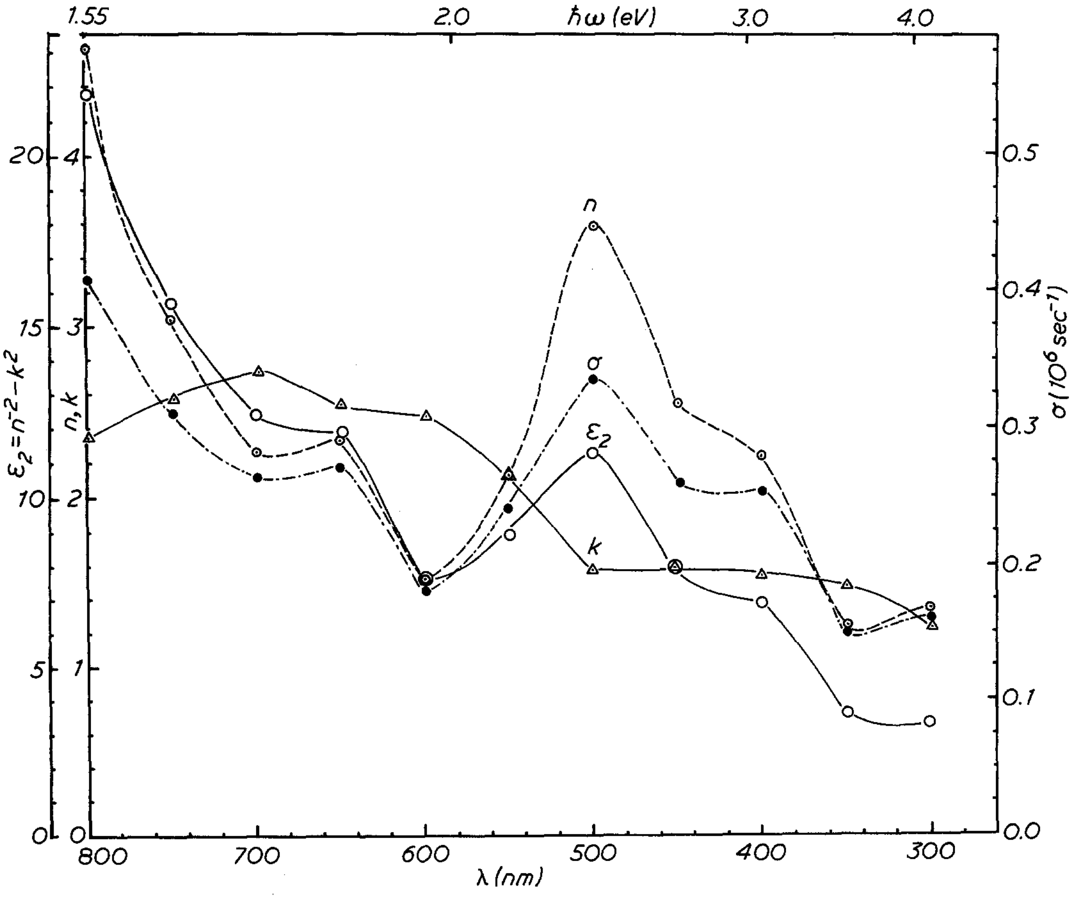

Figure 4 The dependence of the index of refraction (n), the absorption coefficient (k), the imaginary part of dielectric constant (ε_2) and optical conductivity (σ_1) on wavelength.

TABLE II Optical constants for titanium

	λ (nm)	n	k
Present result	450	2.5	1.538
Present result	550	2.1	2.092
Evaporated Ti film [5]	589.2	2.33	3.18
Bulk (0 0 0 1) Ti, air, mechanically polished [17]	540	1.78	1.38
Bulk Ti, air polished [27]	550	1.85	1.7
Bulk (0 0 0 1) Ti, air, chemically polished [17]	540	2.03	1.52
Bulk Ti, air, electropolished [16]	540	2.22	1.31
Ti film prepared in vacuum, measurements in air corrected for oxide [3]	546.1	2.53	1.32
Bulk (0 0 1) Ti cleaned in UHV [28]	546.1	2.96	1.25
Bulk polycrystalline Ti cleaned in UHV [28]	546.1	3.09	1.11
Ti film prepared in UHV [17]	546.1	3.03	1.23
Polycrystalline Ti film [4]	548.6	2.54	3.43
Polycrystalline Ti film [4]	700	2.86	3.96
Present result	700	2.25	2.715

The detailed variation of n, k, ε_2 and σ_1 with wavelength, for the 25 nm sample, is shown in Fig. 4. The values of the optical constants are in reasonably good agreement with the values of Johnson *et al.* [4]. Their values of n and k are slightly larger than the present results at all of their measured energies. Their higher values for the optical constants may result from the measurements being carried out in a nitrogen atmosphere [4]. The present results are given in Table II, together with results of other workers [1, 2, 4, 16, 17, 27, 28]. The results differ from the earlier literature values. Disagreement in the magnitudes of the optical constants reported here is due to problems of sample preparation, accuracy of the optical measurements, and the method by which the experimental data are analysed. Briefly problems of sample preparation arise for mechanically or electrolytically polished bulk samples or slowly evaporated thin film.

The intraband contribution to the dielectric constants can, therefore, be separated from the interband contribution by determining values for the free-electron optical mass and relaxation time at long wavelengths. The optical mass is determined from the long-wavelength slope of a plot of $-\varepsilon_1$ against λ^2 and then the relaxation time from the slope of a plot of ε_2 against λ^2. Such a technique fails for titanium discussed here, because the plots are not linear as required by free-electron theory. Thus it seems that interband transitions contribute significantly throughout the entire spectral range studied here. The present results agree with those of Johnson *et al.* [4].

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