Plasma Resonance in TiO, VO and NbO†

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Reflectance spectra of TiO, VO, and NbO have been recorded. All these oxides show reflectance minima due to plasma edges. The energy corresponding to the reflectance minimum in TiO varies with stoichiometry (in the homogeneity range) and this phenomenon has been related to the transport properties of these oxides.

Plasma oscillations in metallic solids (*1, 2*) can exist as normal modes only if both the real and imaginary parts ϵ_1 and ϵ_2 of the dielectric constant, ϵ, vanish at the plasma resonance frequency, ω_p:

$$\epsilon(\omega_p) = \epsilon_1(\omega_p) + i\,\epsilon_2(\omega_p) = 0.$$

Generally, however, it is sufficient to demand only that $\epsilon_2(\omega_p) < 1$ when $\epsilon_1(\omega_p) = 0$. Reflectance measurements on metals at normal incidence over an extended energy range, followed up by Kramers–Kronig analysis, provide valuable information on the plasma properties of electrons. The reflectance passes through a minimum when both ϵ_1 and ϵ_2 approach zero at ω_p; further, at ω_p the energy loss function $-Im\ \epsilon^{-1}$ shows a sharp peak.

We have examined the reflectance spectra of the monoxides of titanium, vanadium, and niobium in order to search for the possible presence of plasma resonances in these solids, which crystallize in the basic NaCl structure and exhibit high conductivities similar to metals (*3–6*). Both TiO and VO exhibit wide ranges of homogeneity (*5*); accordingly, we have studied the spectra of three rather different compositions of each of these oxides. NbO has a very narrow region of homogeneity (*7*); accordingly, we have examined the spectra of three near-stoichiometric compositions.

Experimental

All the oxides were prepared by melting stoichiometric amounts of high purity metals (> 99.995%

purity) and the corresponding dioxides, sesquioxides or pentoxides (> 99.995% purity) in an arc furnace under an atmosphere of argon gettered with hot titanium (*8*). The compositions of the oxides were established by reoxidation, using gravimetric methods. The lattice dimensions of the oxides were determined by recording powder diffraction patterns with a North American Phillips diffractometer (Cu K_α radiation). The lattice dimensions of all the vanadium and titanium oxides agreed with the literature values (*5*). The unit cell dimensions of NbO_x with $x = 0.98$, 1.00 and 1.02 were 4.2106, 4.2110, and 4.2116, respectively. Four-probe dc electrical conductivity measurements were made wherever feasible.

Reflectance spectra in the 800–210-mμ region were recorded at room temperature employing the reflectance attachment to the Cary Model 14 PMR spectrophotometer. A tungsten lamp served as the light source from 800 to 300 mμ and a hydrogen lamp from 400 to 210 mμ. Reflectance spectra in the 0.3–2.5-μ region were recorded for the titanium oxides employing the improved method described by Sklensky and coworkers (*9*).

Results and Discussion

Titanium monoxide, TiO, shows a sharp reflectance minimum, ω_{min}, at ~3.8 eV (Fig. 1); the reflectance falls nearly to 3% at this energy. The minimum at 3.8 eV was originally assigned to an interband ($t_{2g} - e_g^*$) transition by Companion and Wyatt (*10*), but Denker (*5*) later correlated it with plasma oscillations. The shoulder seen in the
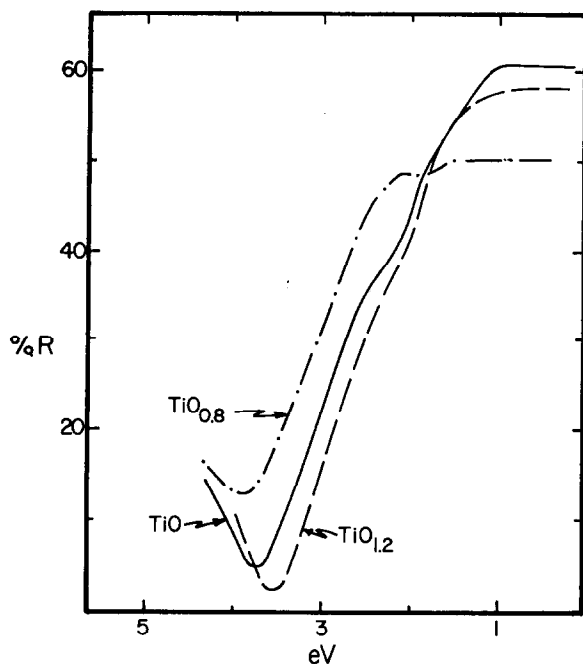
FIG. 1. Reflectance spectra of $TiO_{1.2}$, TiO, and $TiO_{0.8}$.

reflectance spectrum at 2.5 eV (Fig. 1) is, however, likely to be due to an interband transition; understandably, this is at a lower energy than the reflectance minimum due to plasma resonance. The position of the reflectance minimum in TiO_x is quite sensitive to stoichiometry (Table 1 and Fig. 1). Thus, for $x = 1.2$, 1.0, and 0.8, ω_{min} values are observed at 3.6, 3.8, and 4.0 eV, respectively. The appearance of the oxide also changes from yellow bronze to silvery lustre as x decreases from 1.2 to 0.8.

A Kramers–Kronig analysis was carried out numerically on the reflectance data of these titanium oxides, first using a simple exponential extrapolation procedure (11). Subsequently, higher energy dips in the reflectance spectrum were inserted artificially to simulate interband transitions at approximately 7 eV; a special computer program was written for this purpose. The dependence of ϵ_1 and ϵ_2 on energy was found to depend only weakly on the extrapolation methods employed. This agrees with what is commonly observed by workers in this field. With this admittedly approximate procedure it was found that ϵ_1 passed through zero and ϵ_2 was very small in the energy range where the reflectance rapidly decreased. These features are consistent with the interpretation that the change in reflectance of the titanium oxides in the 3–4-eV range arise from plasma oscillations. The variations in the colors of TiO_x are therefore obviously due to the shift in the plasma edge with composition into a different region of the electronic spectrum.

On an elementary model, the plasma frequency and the conductivity is given by,

$$\omega_p^2 = N_c e^2 / m^* \epsilon_\infty$$

and

$$\sigma = N_c e^2 \tau / m^*,$$

where N_c is the carrier density, ϵ_∞ is the optical dielectric constant, and τ is a relaxation time. If τ, m^*, and ϵ_∞ are sensibly independent of composition in TiO_x, then it follows that for two different compositions 1 and 2,

$$(\omega_p^2)_1 / (\omega_p^2)_2 = \sigma_1 / \sigma_2 \approx (100 - R_2)^2 / (100 - R_1)^2,$$

where the equality on the right follows from Ref. (12), R being the reflectance in the near infrared region. Examination of Table 1 shows that the above relations are satisfied by the data. However, one must be careful not to attach too much significance to these findings, since the complications arising from band overlap and the fine distinctions between optical and conductivity effective masses are ignored in the model used here.

Vanadium monoxide, VO, shows the reflectance minimum around 4 eV. ω_{min} occurs at a higher frequency in VO than in TiO; accordingly, the oxide has only metallic lustre but no color. The variation of ω_{min} with x in VO_x is also not as marked as with TiO_x. It seems likely that the minimum in reflectance corresponds to the plasma edge, considering the relatively high conductivities of these oxides. We suspect that the shoulder found at lower energies (~ 2.5 eV) in the reflectance spectra of VO_x is due to an interband transition.

Niobium monoxide, NbO, which has a very high room temperature conductivity (see Table 1) shows

TABLE 1

REFLECTANCE AND RESISTIVITY DATA
ON TiO, VO, and NbO

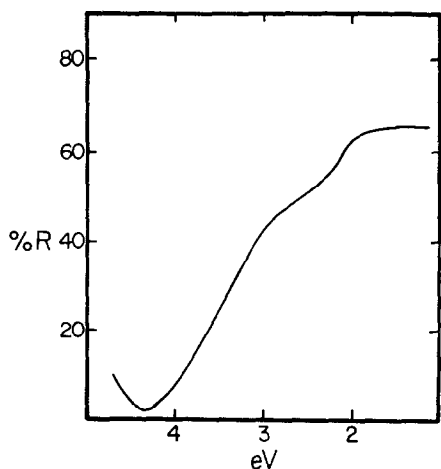| Oxide	ω_{min}, eV (300°K)	R (%) at 1.5 μ (300°K)	ρ, Ω cm $\times$ 10^6 (300°K)
$TiO_{0.8}$	4.00	60	180
TiO	3.80	58	190
$TiO_{1.2}$	3.60	50	260
$VO_{0.8}$	4.00	—	700
VO	3.95	—	800
$VO_{1.2}$	3.85	—	3000
$NbO_{0.98}$	4.35	—	14
$NbO_{1.00}$	4.30	—	20
$NbO_{1.02}$	4.25	—	—

FIG. 2. Reflectance spectrum of NbO.

a sharp reflectance minimum at 4.3 eV as shown in Fig. 2. Using the extrapolation procedure mentioned earlier, the Kramers–Kronig analysis showed that within the uncertainties of the extrapolation, the reflectance minimum at 4.3 eV is associated with a plasma edge. The position of the ω_{min} in the ultraviolet region explains the bright silvery appearance of NbO. Silver metal itself shows the ω_{min} around 4 eV. There is a minor variation of ω_{min} in the narrow range of stoichiometry of NbO_x, with ω_{min} decreasing as the O/Nb ratio is increased.

In conclusion, the optical data shown here are complementary to and reinforce earlier findings that TiO_x, VO_x and NbO_x are oxides which exhibit metallic properties.

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