Optical properties of electron-beam evaporated TiO_2 films deposited in an ionized oxygen medium

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Optical absorption in TiO_2 films depends upon starting material and deposition conditions. The influence of the combined effect of substrate temperature and ionized oxygen on the optical properties of TiO_2 films deposited by reactive electron beam evaporation of TiO is presented. The ionized oxygen medium reduced the absorption in films considerably. The substrate temperature has only marginal influence on the extinction coefficient of these films. The influence of film thickness on the optical properties of TiO_2 films is also studied. The variation in optical properties of TiO_2 films has been explained on the basis of enhanced reactivity of oxygen and the decrease of the condensation coefficient of reacting species at elevated substrate temperature.

I. INTRODUCTION

Multilayer films of TiO_2 and SiO_2 are extensively used in lasers operating in the visible and near IR regions. Optical losses in these films limit the performance of the lasers in both output power and high-power laser damage resistance.[1-4] Electron-beam evaporated SiO_2 films are highly transparent and possess laser damage thresholds comparable to bulk-fused quartz.[5,6] However, TiO_2 films prepared by conventional electron beam evaporation exhibit considerable absorption.' Optical absorption in TiO_2 films depend not only on the preparation techniques but also on the deposition conditions. Studies have been made on TiO_2 films to relate optical as well as structural properties with deposition techniques, as well as deposition parameters.[8-13] Plasma-assisted deposition techniques such as activated reactive evaporation, sputtering, ion plating, ion-assisted deposition, and ion beam sputtering have been employed to obtain films with higher stability and low optical losses.[14-20] Among these techniques activated reactive evaporation is simple, economical, and effective in synthesizing novel compound films. In this technique, the evaporation is carried out in the presence of ionized reactive gas medium.

II. ACTIVATED REACTIVE EVAPORATION

Activated reactive evaporation is carried out in two ways. In the technique developed by Bunshah and Raghuram,[21] the ionization of the evaporant and the reactive gas occurs in the reaction zone which is defined as the space between the vapor source and the substrate. Compound formation takes place in this region. It is a volumetric effect as the process pressure is comparatively higher (10^{-3} mbar). In this technique, low energy electrons are drawn either from the evaporation source or from an auxilary filament and using a biased (20–200 V) electrode in the reaction zone. This process has been employed mainly for tribological coatings and for transparent conducting coatings.

The ARE process developed by Heitmann'' employs a cold cathode discharge source which is mounted inside the deposition chamber. The reactive gas pressure inside the discharge vessel is about 2 mbar while the pressure in the coating chamber is about 1×10^{-4} mbar. This pressure difference is obtained by providing a small hole (0.75 mm diameter) in the outlet capillary tube. The reactive gas passes through this device and gets ionized. The ionized and excited molecules of gas emerge from the nozzle and impinge on the substrate along with the evaporant. The reaction between the evaporant and the ionized gas takes place at the substrate and thereby ensures complete reaction and improves the stoichiometry resulting in the deposition of absorption free films. The energy of the ions is so low that it causes minimum disturbance (dissociation) to the growing film. Ebert[22] reviewed the process of activated reactive evaporation using various currently used discharge sources.

The present day wide beam ion guns differ from the above-said discharge sources in the following points.

(1) Beams are guided; (2) independent control of ion current as well as ion energy is possible; (3) capable of bringing structural changes in the films, apart from improving the stoichiometry.

However, the discharge sources are inexpensive compared to the wide-beam ion guns and at the same time they are effective in lowering the optical losses in the films. Hence this technique is still applicable for the fabrication of low-loss optical thin film devices needed for lasers and laser-based systems.

In our recent paper,' we have reported the optical properties of TiO_2 films deposited by electron beam evaporation of TiO in neutral oxygen. It is observed that TiO_2 films contain considerable absorption despite the favorable deposition conditions. This is explained on the basis of mismatch between the film growth and the reaction rate between evaporant and oxygen. It was also observed that the absorption in TiO_2 films increased with the increase of substrate temperature. Postdeposition heating in air was found to be essential to reduce the absorption in TiO_2 films. In this paper, we report the preparation of TiO_2 films by reactive electron beam evaporation of TiO in an ionized oxygen medium using a Heitmann-type discharge source,'' and study the influence of (a) discharge current in the range 0 to 250 mA (b) substrate temperature in the range 25 to 250 °C, and (c) post-deposition heating of the films in air, on the optical properties of the films for two film thicknesses.

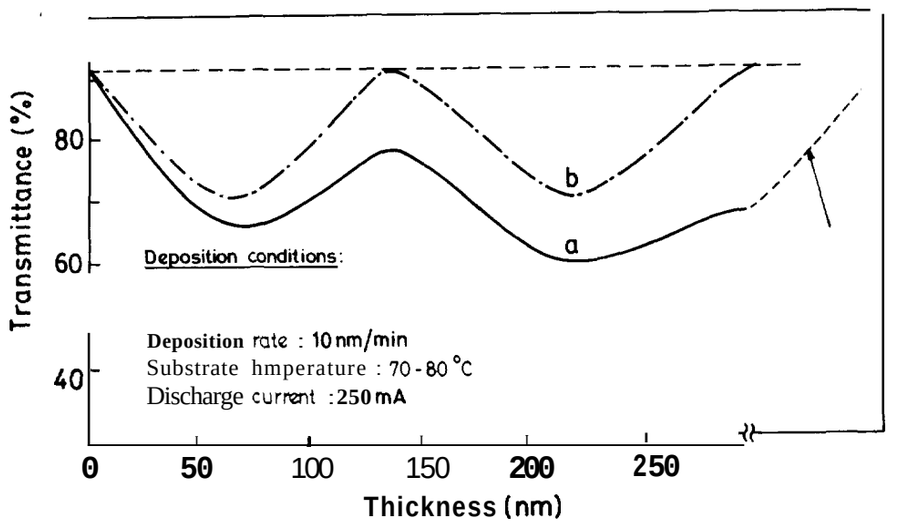

FIG 1. *In situ* optical transmittance of TiO_2 films as a function of thickness for (a) neutral and (b) ionized oxygen.

III. EXPERIMENTAL TECHNIQUES

Titanium dioxide films were deposited in a conventional high-vacuum deposition plant (more details are given in Ref. 7) by electron beam evaporation of TiO (Balzers 99.8%). The discharge source and the electron beam source were mounted opposite each other and symmetrical to the center of the substrate holder. The optimized deposition conditions (obtained through a separate experiment)[23] were (1) rate of deposition, 10 nm /min, and (2) O_2 pressure, 2×10^{-4} mbar. The substrates used were well-polished fused quartz plates of 25 mm diam. and 2 mm thick. These were mounted on a spherical work holder and rotated to get uniform film thickness. The substrates were heated prior to and during deposition using radiant heaters and the required temperature in the range 25 to 250 °C was maintained within ± 5 °C. Film thickness and the rate of deposition were monitored by a quartz crystal monitor (FTM3, Edwards) whereas an optical monitor (OMS2000, Leybold-Heraeus) was used to monitor the quarter-wave thickness as well as *in situ* film transmittance.

The spectral transmittance of the films in air was recorded using a HITACHI 330 model UV visible and near IR double-beam spectrophotometer. The refractive index, extinction coefficient, and thickness of the films were calculated by envelope technique using transmission spectra of the films.[24] Since the films were found to have negligible scattering, it is neglected while estimating the optical constants.

IV. RESULTS AND DISCUSSION

Figure 1 shows the in *situ* optical transmittance of the TiO_2 films as a function of thickness for both neutral and ionized oxygen media. The transmittance maximum at half-wave optical thickness for TiO_2 films is far less than the transmittance of the substrate when neutral O_2 was used indicating that the films are absorbing. It can be seen from curve (b) that the film formed in the presence of ionized oxygen has the transmittance maxima equal to that of the substrate at both half-wave thicknesses. Films exposed to atmosphere also showed similar behavior.

Figure 2 shows the spectral transmittance of TiO_2 films prepared in an ionized oxygen medium with different discharge currents. The absorption in the films (as noted in the difference between the film transmittance maxima at wavelengths corresponding to half-wave optical thickness and the substrate transmittance) decreased with the increase of discharge current. Films deposited at ambient temperature (70 to 80 °C) with a discharge current of 250 mA showed minimum absorption. The reduction of absorption in TiO_2 films deposited in the presence of ionized oxygen may be explained on the basis of an improved reaction between the evaporant and oxygen resulting in well-defined oxides.

Using an optimized discharge current of 250 mA, films were deposited at elevated substrate temperatures. Figure 3 shows the spectral transmittance characteristics of as-deposited films for different substrate temperatures in the range from 50 to 250 °C. It is seen from Fig. 3, that the transmittance maxima of all the films at half-wave optical thickness ($\lambda = 640$ nm) is equal to the substrate transmittance except for the film deposited at 250 °C. More detailed investigations on the influence of substrate temperature on optical transmittance of films is given in subsequent sections.

The refractive index and extinction coefficient of these films are plotted in Fig. 4 as a function of wavelength for as-deposited films. The variation in the refractive index with substrate temperature up to 175 °C was negligible whereas the films deposited at 250 °C showed a higher refractive index as well as a higher extinction coefficient. Upon post-deposition heating at 125 °C in air, the extinction coefficient of this film was also reduced to less than 0.001.

Studies were also pursued on the influence of substrate temperature by carrying out these studies on thinner ($t = 140$ nm) and on thicker films of TiO_2 ($t = 280$ nm) by keeping the substrate at different temperatures during deposition. The results on optical transmittance maxima (at

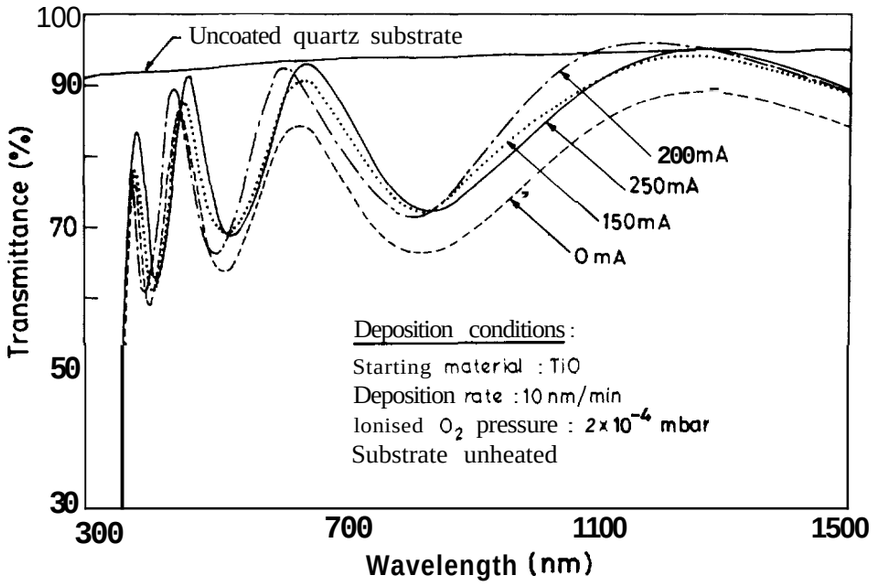

FIG. 2. Measured spectral transmittance of as-deposited 290 nm thick TiO_2 films for different discharge currents.

$\lambda = 640$ nm) of TiO_2 films for both the thicknesses as a function of substrate temperature are summarized in Fig. 5. (These data were collected from the spectral transmittance characteristics of the films in air). In the case of thicker films the transmittance of the films was recorded by keeping the bare substrate in the reference beam.

In general there is a decrease in transmittance of the films with increase in substrate temperature. The decrease in transmittance of films with increased substrate temperature might be due to insufficient oxygen incorporation in the films during deposition at elevated substrate temperatures, as the condensation of oxygen decreases at higher substrate temperatures, which also has been observed by Ritter and others.' Kuster and Ebert[14] also observed an increase of absorption in TiO_2 films with the increase of substrate temperature both for neutral and ionized oxygen. They have

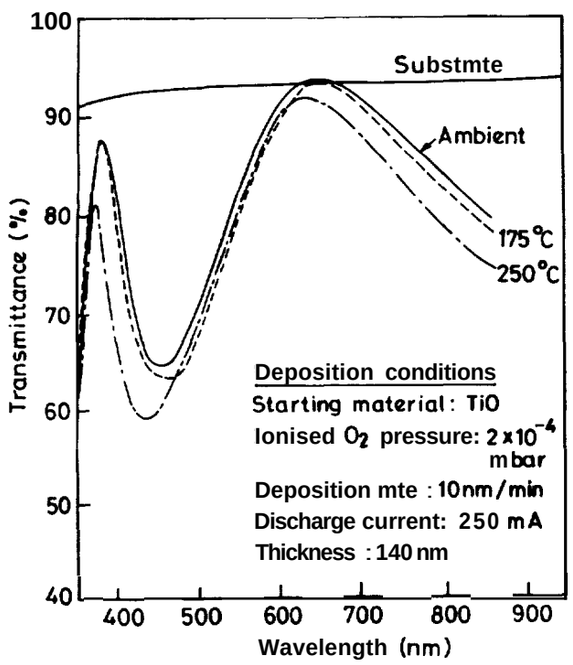

FIG. 3. Measured spectral transmittance of as-deposited TiO_2 films for different substrate temperatures.

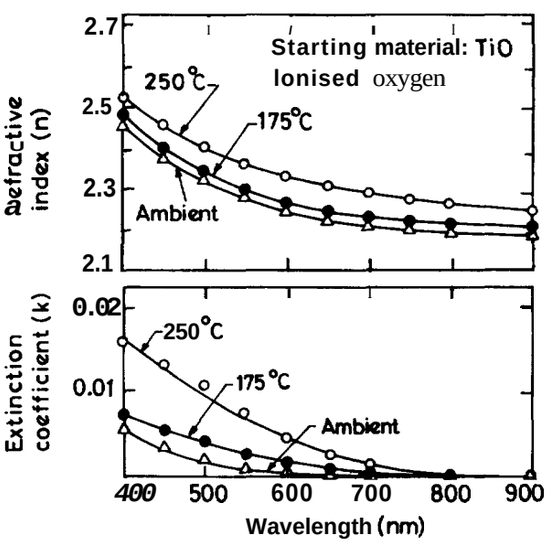

FIG. 4. Calculated optical constants (n and k) of TiO_2 films for different substrate temperatures as a function of wavelength.

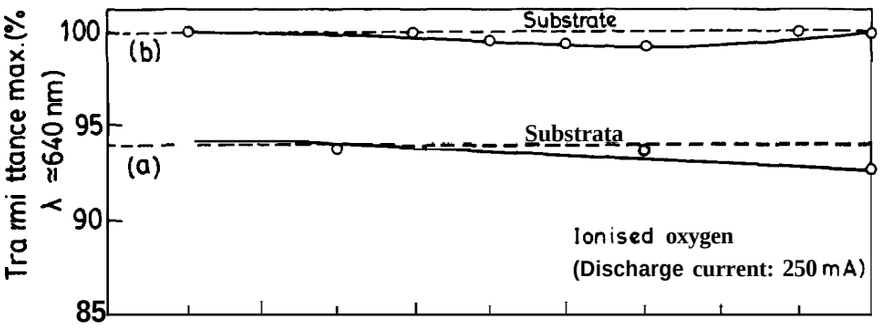

FIG. 5. Transmittance maximum at 640 nm of TiO_2 films as a function of substrate temperature for a thickness of (a) 140 nm and (b) 280 nm.

explained it on the basis of decomposition of TiO_2 at elevated substrate temperature.

However, both thicker and thinner films showed higher transmittance even at elevated substrate temperatures when ionized oxygen was used in comparison with neutral oxygen.' Despite the decrease of oxygen content with substrate temperature, the films showed higher transmittance due to the improved reaction between the ionized oxygen and the evaporant. This observation also agrees with Heitmann's[25] results in the case of SiO_2 films that 20 to 100 oxygen molecules are required for every SiO molecule in the case of neutral oxygen whereas using ionized oxygen about ten molecules are sufficient for complete oxidation.

The lower absorption found in the case of thicker films deposited at elevated temperature (> 200 °C) is observed for the first time. This could be due to the temperature influencing the condensation coefficient of both oxygen and titanium. Pulker et *al.*[13] observed that a significant amount of titanium is present in vapor when TiO is evaporated. However it needs more detailed investigations to explain this behavior. Further work in this direction is under progress.

Preliminary investigations made on the chemical composition of a few TiO_2 films using x-ray photoelectron spectroscopy revealed that the stoichiometry of the film was a mixture of Ti, O, and TiO_2 when neutral oxygen was used at ambient temperature. The Ti, O, content decreased considerably when an ionized oxygen was used for the same deposition conditions. It is observed that the film composition is completely TiO_2 when the substrate temperature is 250 °C in ionised oxygen (discharge current of 250 mA). This confirms the earlier observation that the improved transmittance in films deposited at higher temperatures (> 200 °C) is due to improved stoichiometry of the films. Incidentally these films also showed crystallinity (x-ray diffraction) in the case of thicker films. More detailed study on film composition and structure with preparation conditions is under progress and will be reported later.

The refractive index and extinction coefficient of the as-deposited films for both the thicknesses are presented in Table I. The refractive index of the films increased only marginally up to 175 °C for thinner films. It is also seen that the thicker films showed higher refractive indices than did the thinner ones and increased with the increase of substrate temperature. The increase of the refractive index at higher substrate temperature may partly be due to the improved packing density and also due to the onset of crystallinity in films.

TABLE I. Calculated optical constants (n and k at 640 nm) of as deposited TiO_2 films with substrate temperature.

Substrate temperature (°C)	t = 140 nm		t = 280 nm	
	n	k	n	k
Ambient	2.22	0.001	2.20	0.001
100	2.22	0.001	2.27	0.001
175	2.24	0.001	2.31	0.001
250	2.30	0.002	2.34	0.001

IV. CONCLUSIONS

It has been demonstrated that low-loss durable and stoichiometric TiO_2 films can be deposited using a Heitmann-type discharge source by conventional reactive electron beam evaporation of TiO. A discharge current of 250 mA was found to be necessary for completely oxidizing the film. The primary effect of the ions is only to improve the stoichiometry of the film and this has negligible effect on the refractive index. On the other hand, increasing the substrate temperature has improved the refractive index of the films without affecting the extinction coefficient. Film thickness has influenced both the refractive index and the extinction coefficient of the films. The increase in thickness resulted in an increase of the refractive index and oxidation in the films.

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