Annealing effect on ion-beam-sputtered titanium dioxide film

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We found that the extinction coefficient of ion-beam-sputtered titanium dioxide films first decreased with increasing annealing temperature then increased drastically when annealing temperature was increased above 200 °C for 24 h of annealing time. The decreasing extinction coefficient with annealing temperature was attributed to a reduction in absorption owing to oxidation of the film by annealing. The film structure remained amorphous to 200 °C annealing temperature. The drastic increase of extinction coefficients above 200 °C was associated with the appearance of an anatase polycrystalline structure and was attributed to scattering by the polycrystalline structure. With shorter annealing time the transition temperature from amorphous to polycrystalline anatase was higher. Guidance for reducing the optical loss of laser mirrors is proposed. © 1998 Optical Society of America

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Reduction of optical loss for high-reflectance dielectric mirrors is crucial to applications such as high-energy lasers and ring laser gyroscopes. Titanium dioxide (TiO₂) film is the most commonly used high-refractive-index material in the multilayer dielectric mirror. The optical properties of TiO₂ films are delicately dependent on the fabrication process and other factors. The ion-beam-sputter method was reported to produce dielectric mirrors with lower loss than other deposition methods. Annealing of a dielectric mirror after deposition is a common practice to reduce the optical loss of the mirror. However, to our knowledge there has been no report on the loss-reduction mechanism of annealing, in that this process seems to be a craft rather than a scientific practice. In this Letter we report the results of our systematic studies of the annealing effect on optical loss of ion-beam-sputtered TiO₂ films. We also provide a deeper understanding of the mechanism of loss modification by annealing.

We used a Kaufmann-type 2.5-cm ion gun (Ion Tech Inc.) to sputter deposit TiO₂ films. The sputter parameters were 1-kV beam voltage and 50-mA beam current; we used a plasma bridge neutralizer to neutralize the output ion gun. The sputter target was a 10-cm-diameter Ti target of 4N purity. The baseline vacuum level was 1.5 × 10⁻⁶ torr, the Ar partial pressure was 3 × 10⁻⁴ torr, and reactive sputtering was carried out in 3.7 × 10⁻⁴ torr O₂ partial pressure. The films were deposited upon Balzers BN845432-T soda lime glass substrates of 1.2-mm thickness and 2.5-cm diameter.

All samples under investigation were deposited at room temperature with exactly the same deposition conditions and 80-min deposition time, the films thickness were ~380 nm. After deposition each sample was annealed at a different constant temperature for 24 h. The annealing process was carried out in a furnace with atmosphere environment.

The transmission spectrum in the wavelength range 190–800 nm was measured for each sample after annealing. The refractive index and the extinction coefficient of the films were deduced from the transmission spectrum in the wavelength range 400–800 nm by use of Swanepoel’s method. Within this range the extinction coefficient of the film is small, such that Swanepoel’s method is valid. Glazing-angle x-ray diffraction measurements were taken for each sample to determine the structure of the films before and after annealing. Atomic force microscopy (AFM) was used to investigate the surface morphology and to determine the rms surface roughness of the samples.

The transmission spectrum measurements were carried out with a Hitachi U-3410 spectrophotometer. The precision of the transmission measurement was ~0.1% in transmittance after sufficient warming up of the instrument. The standard deviation as determined from the transmission spectrum with Swanepoel’s method was found to be less than 0.01 for the refractive index (n) and less than 0.0001 for the extinction coefficient (k).

Table 1 shows n and k at wavelengths of 632.8, 550, and 450 nm for films after they were annealed at various temperatures for 24 h. Table 1 shows that n remains unchanged below 200 °C and decreases slightly above 200 °C, whereas k decreases with increasing temperature to 200 °C, then increases drastically with temperature above 200 °C. The intrinsic absorption edge of stoichiometric TiO₂ was known to be near ~400 nm. Therefore, within the precision of our measurement, variation of k with annealing temperature is more profound at short than at long wavelengths.

We found from x-ray diffraction that films that were subjected to annealing at temperatures below 200 °C for 24 h, as well as the as-deposited film, were all amorphous in structure. TiO₂ anatase peaks started to appear for films subjected to annealing above 200 °C for 24 h. The x-ray diffraction peak intensity increased with the annealing temperature and saturated at ~275 °C. At this temperature crystallization of anatase phase was complete. The relative intensity of the TiO₂ anatase (101) diffraction peak, which is the strongest diffraction peak, is shown in Table 1 for each sample. From these data we conclude that the room-temperature ion-beam-sputtered TiO₂ film is amorphous and that there is a phase transition from amorphous to polycrystalline anatase at 200 °C for 24-h annealing; the transition is complete at ~275 °C for 24-h annealing. It is clear from Table 1 that the onset
Table 1. Refractive Index \((n)\) and Extinction Coefficient \((k)\) at Wavelengths of 632.8, 550.0, and 450.0 nm for an Annealing Time of 24 h

<table>
<thead>
<tr>
<th>Annealing Temp. ((^\circ C))</th>
<th>632.8 nm (n)</th>
<th>632.8 nm (k)</th>
<th>550.0 nm (n)</th>
<th>550.0 nm (k)</th>
<th>450.0 nm (n)</th>
<th>450.0 nm (k)</th>
<th>(I_0/I_0^a) (%)</th>
<th>(\lambda_c^b) (nm)</th>
<th>rms Surface Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before annealing</td>
<td>2.50</td>
<td>0.0001</td>
<td>2.54</td>
<td>0.0003</td>
<td>2.66</td>
<td>0.0013</td>
<td>0</td>
<td>327.6</td>
<td>0.12</td>
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<tr>
<td>150</td>
<td>2.50</td>
<td>(&lt;10^{-4})</td>
<td>2.54</td>
<td>0.0002</td>
<td>2.66</td>
<td>0.0012</td>
<td>0</td>
<td>325.0</td>
<td>0.15</td>
</tr>
<tr>
<td>200</td>
<td>2.50</td>
<td>(&lt;10^{-4})</td>
<td>2.54</td>
<td>0.0001</td>
<td>2.66</td>
<td>0.0010</td>
<td>0</td>
<td>322.4</td>
<td>0.14</td>
</tr>
<tr>
<td>225</td>
<td>2.49</td>
<td>0.0001</td>
<td>2.53</td>
<td>0.0002</td>
<td>2.65</td>
<td>0.0011</td>
<td>20</td>
<td>319.2</td>
<td>0.84</td>
</tr>
<tr>
<td>250</td>
<td>2.48</td>
<td>0.0004</td>
<td>2.52</td>
<td>0.0007</td>
<td>2.64</td>
<td>0.0023</td>
<td>65</td>
<td>316.5</td>
<td>1.34</td>
</tr>
<tr>
<td>275</td>
<td>2.48</td>
<td>0.0007</td>
<td>2.52</td>
<td>0.0012</td>
<td>2.64</td>
<td>0.0040</td>
<td>100</td>
<td>313.8</td>
<td>1.72</td>
</tr>
<tr>
<td>300</td>
<td>2.48</td>
<td>0.0015</td>
<td>2.52</td>
<td>0.0025</td>
<td>2.64</td>
<td>0.0052</td>
<td>100</td>
<td>313.5</td>
<td>3.26</td>
</tr>
<tr>
<td>350</td>
<td>2.48</td>
<td>0.0018</td>
<td>2.52</td>
<td>0.0027</td>
<td>2.64</td>
<td>0.0062</td>
<td>100</td>
<td>313.5</td>
<td>3.30</td>
</tr>
</tbody>
</table>

\(^a\)Relative x-ray intensity for the TiO\(_2\) anatase (101) diffraction peak.

\(^b\)Cutoff wavelength.

of a drastic increase in \(k\) is associated with the phase transition from amorphous to polycrystalline anatase.

Figure 1 shows an AFM picture of the film annealed at 300 \(^\circ\)C. 256 \(\times\) 256 points were taken in the 1 \(\mu\)m \(\times\) 1 \(\mu\)m scanned area for this picture. The roughened polycrystalline surface is clearly shown. AFM pictures of the samples with amorphous structure with the same resolution as that of Fig. 1 showed a structureless and smooth surface. The rms surface roughnesses obtained from high-resolution AFM scanning for all samples are listed in Table 1. The precision of the rms roughness measurements from AFM was found to be 0.04 nm. It is clear that the drastic increase in \(k\) was not only associated with the appearance of polycrystalline anatase phase, as was suggested by x-ray diffraction, but also was associated with the drastic increase in surface roughness of the polycrystalline structure.

We found from the AFM picture of the 350 \(^\circ\)C annealed sample, besides the polycrystalline structure, that profound wrinkles in scales larger than that of Fig. 1 also showed up as a result of high-temperature annealing. The wrinkles enhanced the roughness of the surface. Therefore, increasing \(k\) is associated not only with the surface roughness of the polycrystalline structure but also with wrinkling of the film at high annealing temperature, whereas x-ray diffraction peaks indicate only the appearance of polycrystalline but not the wrinkles.

Figure 2 shows the transmission spectra at short wavelengths for the samples. For clarity only spectra for samples annealed at three representative temperatures are shown. The transmittance edge shifts to a shorter wavelength with increasing annealing temperature, indicating lower optical extinction for samples annealed at higher temperature. The inset of Fig. 2 shows the spectra close to zero transmittance. The wavelength at which the transmittance is zero is defined as the cutoff frequency \((\lambda_c)\). \(\lambda_c\) for all samples are listed in Table 1.

It is known\(^5,6\) that the total integrated scatter of a rough surface is, in general, proportional to \(\sigma^2/\lambda^2\), where \(\sigma\) is the rms surface roughness. The high-temperature annealed samples with high surface roughness are supposed to have higher scattering loss at short wavelengths than that of the low-temperature annealed samples, but the trend of higher transmittance (i.e., lower optical extinction) for high-temperature annealed samples at short wavelengths as shown in Fig. 2 indicates that optical...
Extinction in the short-wavelength region is absorption dominant rather than scatter dominant. Therefore $\lambda_c$ can be considered as a qualitative indicator of the degree of absorption. A lower $\lambda_c$ corresponds to lower absorption. $\lambda_c$ in Table 1 shows that the absorption loss is reduced with increasing annealing temperature then remains constant above $\sim 275$ °C annealing temperature.

We assert that as-deposited TiO$_2$ films are oxygen deficient such that in the energy bandgap of the stoichiometric TiO$_2$ there are oxygen-deficient electronic energy states in the energy bandgap near the band edge. Therefore the optical transmittance edge of the as-deposited TiO$_2$ shifts to a longer wavelength than that of the stoichiometric TiO$_2$. The effect of annealing is to enhance the oxidation such that the oxygen-deficient energy states are eliminated and the transmittance edge shifts back toward a shorter wavelength, as indicated in Fig. 2.

Extinction coefficient $k$ can be divided into two parts, absorption coefficient $\alpha_a$ and an equivalent distributive scattering coefficient, $\alpha_s$:

$$k = \alpha_a + \alpha_s.$$  \hspace{1cm} (1)

In the long-wavelength region, near 632.8 nm in particular, within which the absorption and scattering coefficients are small and hard to measure but are crucial to many applications, the relationships among $k$, $\alpha_a$, $\alpha_s$, and annealing temperature can be qualitatively deduced from previous discussions on data in Table 1 and are illustrated schematically in Fig. 3. Because of oxidation, $\alpha_a$ decreases with increasing annealing temperature and then becomes saturated. $\alpha_s$ is small compared with $\alpha_a$ and remains at a constant low annealing temperature owing to the amorphous structure of the film. $k$ is dominated by $\alpha_a$ at low annealing temperature. $\alpha_s$ increases drastically near the phase-transition temperature at which the structure changes from amorphous to polycrystalline TiO$_2$ anatase phase and dominates $k$ above the transition temperature.

We also found that for a shorter annealing time (3 h) the onset of the phase-transition temperature was shifted to $\sim 250$ °C, and the transition was completed at $\sim 275$ °C. The phase-transition temperature is higher and the temperature range for the phase transition to proceed to the full extent is smaller for a shorter annealing time.

We have made quarter-wave multilayer stacks of TiO$_2$/SiO$_2$ mirrors. The variation of the total loss, i.e., absorption loss plus scattering loss, of the multilayer stacks with annealing temperature followed the trend of the $k$ curve in Fig. 3. SiO$_2$ film is much less absorptive than TiO$_2$ and does not crystallize in our annealing temperature range, which implies that the annealing characteristics of single-layer TiO$_2$ film persist in the multilayer stack. Therefore Fig. 3 serves as a general guide for reducing the total loss of a laser mirror by annealing: First, it is possible to reduce the total loss of an ion-beam-sputtered laser mirror that contains TiO$_2$ as the high index layer by use of thermal annealing. But there are optimum annealing temperature and time that one has to choose carefully to avoid an increase of scattering loss owing to crystallization when the absorption loss is reduced by annealing. Second, one can manipulate the deposition and annealing conditions to change the magnitudes of $\alpha_a$ and $\alpha_s$ to reduce the total loss. For example, deposition or annealing in a higher-oxygen-content environment will shift the $\alpha_a$ curve to the left, and the total loss of the mirror that has been annealed under the optimized condition will be dominated by scattering loss, which is related to the roughness of the amorphous structure and hence to the surface roughness of the substrate. Deposition at high temperature will shift the $\alpha_s$ curve to the left, which is not desirable. It is also possible to mix TiO$_2$ film with additives to increase the crystallization temperature such that the $\alpha_s$ curve shifts to the right, and the mirror could sustain a higher annealing temperature to reduce $\alpha_s$ further without crystallization. We also believe that, in general, the annealing characteristics of TiO$_2$ films will be applicable to other oxide materials such as tantalum oxide film for which the as-deposited film structure is amorphous.

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References