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OPTICAL PROPERTIES OF OXIDE COATINGS PREPARED BY ION-ASSISTED DEPOSITION[1]

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ABSTRACT

An investigation was made by changing the preparation parameters, such as different ion species, ion energy, and ion current density, etc., to determine their effects on refractive indices, absorption, and laser-induced damage threshold, etc. of the coatings of TiO_2, ZrO_2 and SiO_2 whose oxide coatings were prepared by ion-assisted deposition.

1. INTRODUCTION

Ion current assisted deposition (IAD) is done with ions shot out of an ion source to bombard the growing coating, and the collision of the ions activates the activation energy of the growing coatings to raise the atomic absorption transition rate and thus promotes chemical activities. Because the preparation of coatings with the IAD technique increases the deposition density and can optimize the chemical composition ratios, the refractive indices of the coatings are improved, the absorption is reduced, and the stability and toughness of the coating are enhanced [1-4].

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[1] Received the draft on June 7, 1990, and received the revised draft on October 4, 1991.

* Numbers in margins indicate foreign pagination. Commas in numbers indicate decimals.

In using the IAD technique to prepare coatings, one can easily control and manipulate various preparation parameters, such as the ion current density, the ion collision angles and ion species, etc. and thus one can quite easily control and vary the working conditions to obtain some specifically required coatings. This paper studies various kinds of ions (oxygen ion, mixture of argon-oxygen ions, and argon ion), and the effects of the different ion species, their ion energies, and ion current intensities, etc. on optical properties of the coatings of TiO_2, ZrO_2 and SiO_2 prepared by ion-assisted deposition, such as refractive indices, optical absorption and laser-induced damage threshold values, etc. It thus establishes and acquires the IAD technique conditions for a superior quality of optic coatings.

2. EXPERIMENTAL APPARATUS

The deposition of coatings was carried out inside an inverted bell-shaped cover of 1 m in diameter on a coating stand, the vacuum structure is shown in Fig. 1, a Kaufman ion gun with muzzle diameter of 8 cm provided the neutral ion current to bombard the substrate in the vertical direction. The ionic energy can be adjusted within the range of 300 ~ 1,000 eV, and to do this in the vicinity of the substrate a Faraday prober was installed to control the ionic current intensity reaching the substrate. The 3 kinds of materials, namely TiO_2, ZrO_2 and SiO_2, are the subjects for sublimation coating with an E-shaped electron gun used for single layer coatings, and the wavelength controlling the coating thickness was 632.8 nm. The parameters of this equipment are shown in Table 1. The active gases used in the ion gun were either pure oxygen, pure argon, or a mixture of oxygen with argon at ratios of 3:7 or 7:3, to investigate the effects of all these ions with all different compositions on the optical properties of the coatings.

In calculating the refractive indices of the coatings, the transparency of the thickness and the spectra of the reflected light, a spectrogram was used.

The coating absorption was measured, as shown in Fig. 2, with the instrument for weak absorption measurements of the optico-thermal conversion method, and the sensitivity of this instrument could reach the order of 10^{-5}.

The laser-induced damage threshold value by a single pulse laser was measured at wavelength of 1.06 micron, and it was carried out on a YAG laser of pulse width of 10 ns.

3. RESULTS

1. Refractive Indices

In Fig.3 the curve shows the change in refractive index of TiO_2 coating of the IAD deposition with respect to the ion energy, and the assisting ions were oxygen ions; at the beginning the refractive index of TiO_2 of IAD rose as the ion energy increased, and the larger the ion current intensity was, the larger became the increment width of the refractive index, but when the ion energy reached a certain critical value the refractive index obtained its maximum value. When the ion energy exceeded this critical value the refractive index of the coating went below the refractive index of the deposited coating by the ion energy at its critical value; for different ion current intensities the critical values of the ion energies varied, but the larger the current intensity was, the lower was the critical value of the ion energy.

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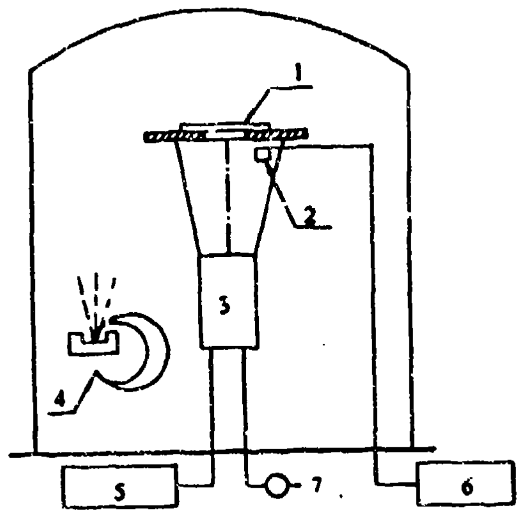

Fig. 1 Configuration of deposition system

Key: 1. Substrate; 2. Faraday prober; 3. ion source; 4. electron gun; 5. ion gun power supply; 6. galvanometer; 7. inserted gas

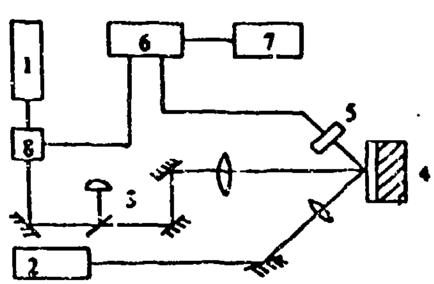

Fig. 2 Configuration of absorption measurement

1. pump laser; 2. probe laser; 3. power monitor; 4. sample; 5. position sender; 6. lock-in amplifier; 7. oscilloscope; 8. A-O modulator

Table 1 Deposition parameters

meterial	TiO_2	ZrO_2	SiO_2
deposition rate / $(nm \cdot s^{-1})$	0.6 ~ 0.7	0.5	0.5
substrate temperature/ ℃	50	50	50
pressure of O_2 / Pa	1.2×10^{-2}	2×10^{-2}	$<10^{-3}$
optical thickness	λ/4	λ/4	λ/4

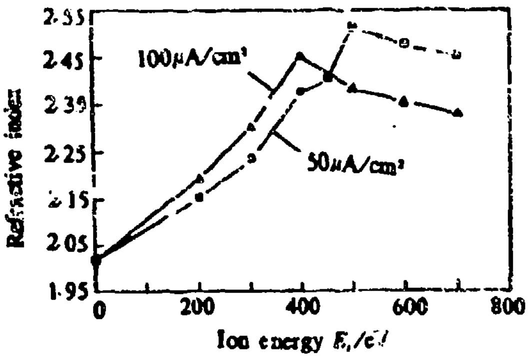

Fig. 3 Refractive index of TiO_2 films bombarded with O_2+ as a function of ion energy

As shown in Fig. 4, the characteristic of the refractive index of the IAD TiO_2 film with respect to the ion current intensity was similar to that with respect to the change of the ion energy. One can find out whether the ion current intensity has reached a critical value by determining whether the refractive index of the deposited coating has reached its maximum value, while one can determine whether the energy current intensity has reached its critical value by watching the increase of the ion energy followed by the initiation of a decrease.

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The ZrO_2 film (with argon-oxygen ratio of 7:3) by the IAD deposition exhibits the above-mentioned characteristics of the refractive index with respect to the ion energy and ion current intensity.

Recently, the simulation of the effect of ion bombardment on film growth has produced many results [5,6], and among them the most successful simulation was to use a duo-element collision and molecular dynamics to explain the densification of the film coating by ion-assisted deposition. The densification of an IAD film is accomplished by the process of ion-participating coupling along with the reactive impact of surface atoms to make an implant. The result of the simulation clarified the following few points : When the ion energy increased, the probability of the appearance of the phenomenon of reactive impact for the implanting also increased; the probability of ion participation increased when the ion current intensity increased; the refractive index of the film was mainly determined by the density of the film; and the change in refractive index corresponded to the reaction to the change of the film density. Thus as the ion current density increased, the refractive index expanded the increment width with respect to the ion energy increase; for the refractive index to reach the maximum value it needed the ion energy at the critical value but afterwards it dropped off again (Fig. 3); in the same fashion one can also explain the phenomenon (Fig. 4) that the ion current intensity reached a critical value with an increase of the ion energy but then it dropped down again; when both the ion energy and the ion current intensity were at the critical values, except to generate ion-participating couplings and the reactive impact implants, the phenomenon in which the deposited atoms could splash up the film layer appeared and thus diluted the film, and the increase of both the ion energy and current intensity could increase the probability of such atomic splashing. Thus for a given coating material, there is a unique set of values for the ion energy and ion current intensity which alone could make the refractive index reach its maximum value.

We studied the bombardments with various different ion species to investigate their effects on the refractive indices; Fig. 5 shows the cases in which oxygen ions were used to make the bombardments, and also when the mixture of argon-oxygen at a ratio of 3:7 was used for the bombardment the curve of change in the refractive index with respect to the ion energy is shown. The ion current intensity was always kept at 50 $\mu A/cm^2$. One can see that the critical value of the ion energy when the oxygen ion was used is higher than that when the mixture ions were used for the bombardment. This was because for the same ion energy the atomic weight of argon is greater than that of oxygen, and thus the momentum of argon ions was greater than that of oxygen ions; the bombardment with the argon ions created a slightly larger probability for the reactive impact implant than the case of using oxygen ions, and consequently, when the mixture of argon ions is used, one needs a lower critical value for the ion energy than is the case for using pure oxygen in the ion-assisted deposition.

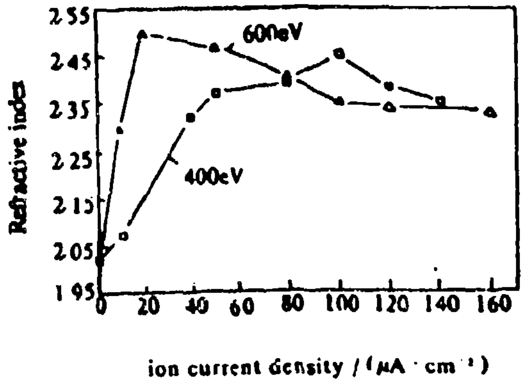

Fig. 4 Refractive index of TiO_2 films bombarded with O_2+ as a function ion current density.

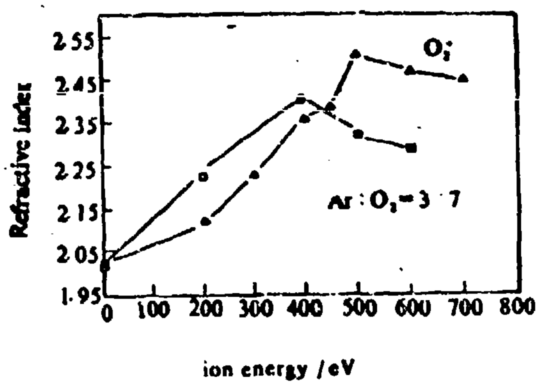

Fig. 5 Refractive index of TiO_2 films bombarded with different ions

As can be seen from Fig. 6, for the case of ZrO_2 films, use of the mixture ion of argon-oxygen at a ratio of 7:3 gave a much better effect than in the case of using pure oxygen. In the former case for an ion energy of 800 eV, the refractive index could already reach its maximum value; while using oxygen alone required much higher ion energy as well as ion current density [7]. Fig. 7 covers the case of the SiO_2 films of the ion-assisted deposition, to show the curve of change in refractive index with respect to the ion energy.

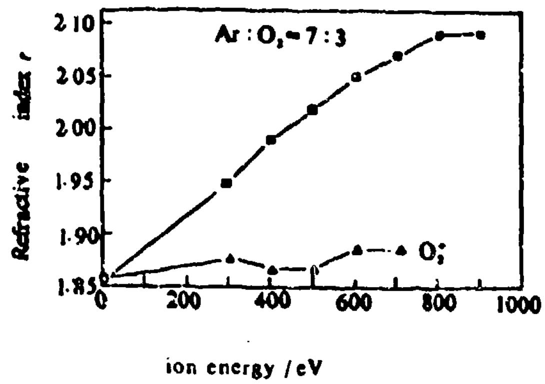

Fig. 6 Refractive index of ZrO_2 films bombarded with different ions.

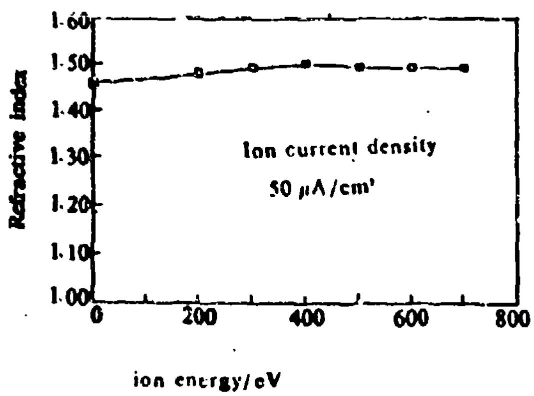

Fig. 7 Refractive index of SiO_2 fims bombarded with mixture ions ($Ar:O_2$ = 7:3)

2. Absorption

It is very clear that the ion-assisted deposition has an effect on the absorption characteristics of the TiO_2 film; when argon and oxygen ions at a ratio of 7:3 were used to bombard the TiO_2 film, even a very low ion energy could create a strong absorption, as shown in Table 2, but the absorption became even larger as the ion energy and current intensity became large. When pure oxygen or a large concentration of oxygen in the argon-oxygen mixture (argon-oxygen ratio at 3:7) were used in bombardments, there was a noticeable decline in the film absorption, and thus even if the ion energy rises, one still can maintain a low absorption. When the ion current density rises, the film absorption undergoes a rapid decline.

Table 2. Effect of different ion bombardments on absorption of TiO_2 coatings

ion	ion energy /eV	ion current density/ ($\mu A \cdot cm^{-2}$)	extinction coefficient
Ar	200	50	$>10^{-3}$
$Ar:O_2$ 7:3	300	50	9.0×10^{-3}
	500	50	3.0×10^{-3}
	500	100	6.4×10^{-3}
$Ar:O_2$ 3:7	300	50	2.8×10^{-4}
	400	50	3.8×10^{-4}
	500	50	4.0×10^{-4}
	600	50	3.5×10^{-4}
O_2	300	50	2.8×10^{-4}
	400	50	3.4×10^{-4}
	500	50	3.6×10^{-4}
	500	100	1.5×10^{-4}
	600	50	3.2×10^{-4}
	600	100	2.2×10^{-4}
unbombarded	0	0	1.4×10^{-3}

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The properties of film absorption are intimately related to the chemical composition ratio. In speaking of oxide coatings, when the composition of oxygen is low the film exhibits a large absorption. In general when a coating is formed by distillation of TiO_2, the chemical activation is not enough, and for a low oxygen content absorption is relatively large. For the IAD deposited TiO_2 film, the ion bombardment can change the chemical composition ratio of the film. On the one hand, the ion bombardment can first splash up the oxygen atoms; on the other hand, if an ion of high oxygen concentration is used for bombardment, ionic oxygen can promote the chemical activation of the film, and thus Ti can be sufficiently oxidized to raise the composition of oxygen. Using ions with a low concentration of oxygen assists film deposition, and not only absorption is large but it increases further when the ion energy and current density increase. When ions of high concentration of oxygen are used in assisting film deposition, the ionic oxygen energy can sufficiently replace the splashed up oxygen to lower the absorption; by increasing the ion current density one can deposit out films with rich oxygen contents to make a rapid decline of absorption.

For the IAD deposited ZrO_2 films, when pure oxygen was used in bombardment, the ions first splashed the oxygen atoms, and the absorption was larger than the film of a distilled deposition; by use of the argon-oxygen ratio of 7:3 in assisting deposition for the ZrO_2 films, absorption declined, as compared to the film by distillation deposition.

3. Laser-Induced Damage Threshold Value (LIDT)

Table 3 shows the laser-induced damage threshold values of TiO_2 films due to various different assistance deposition conditions, and the values shown in the table are the relative ratios with respect to the films which did not have any assistance. One can see that the LIDT value of pure oxygen assisted deposition is slightly higher than that without any assistance; when the ion energy goes up, the LIDT value goes down. The LIDT value of the ion assisted deposition mixture with argon-oxygen ratio of 3:7 is almost the same as those without any assistance, but when the ion energy goes up it goes down rapidly.

For the ZrO_2 film of the ion assisted deposition mixture with argon-oxygen ratio of 7:3, the LIDT value drops down rapidly as the ion energy rises, as shown in Table 4.

Table 3. LIDT's of TiO_2 films deposited by IAD in the case of ion current density at 50 $\mu A/cm^2$

ion energy /eV	300	400	500	600
$Ar:O_2=3:7$		1.05	0.91	0.87
O_2	1.24	1.08	1.09	1.08

Table 4 LIDT's of ZrO_2 films deposited by IAD

ion energy /eV	200	300	600	700
ion current density $/(\mu A \cdot cm^{-2})$	20	50	100	100
LIDT	1	0.86	0.84	0.69

The experimental results clarified the following few points: By use of low energy, oxygen ion assisted bombardment in growing the films, one can raise the laser-induced damage threshold value of the oxide coatings.

Many things car affect the characteristic laser-induced damage threshold of films, but they can be classified into 2 kinds: local properties and whole-body properties. The local properties of the commonly created damages are ordinary defects in the film; such defects can include major defects, such as scratch marks, splashed over dirts. Minor defects are chemical contaminatious, mixed boundaries, color centers, damaged ridges, etc. Minute defects are in general due to the deficiency existing in the coating techniques. The whole-body properties include optical characteristics, such as refractive indices, and mechanical properties, such as stress, rigidity coefficient, deposit density, surface coarseness or adhesiveness, etc.; thermal properties, such as thermal conductivity and thermal capacity, etc.; chemical properties, such as chemical composition ratio and chemical mixture materials, etc.; even the system structure and fine structure of the film can be factors of the whole-body properties which would affect the laser-induce. damage threshold values.

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For the films of ion-assisted deposition, the film layer density can be raised, the chemical composition ratio and film fine structure can be improved, absorption can be lowered, the stability and rigidity of the film can be enhanced, and thus the film of pure oxygen ion assisted deposition can be used to raise the laser-induced damage threshold value at a low ion energy. In a situation of high ion energy, the film can be contaminated by all kinds of impurities, such filament fragments of the ion gun or debris of the ion gun to contaminate the film band; the film grown by some high energy ion bombardment can also allow defects between film granules, which exacerbates microscopic defects to the films and lowers the laser-induced damage threshold values of the film. For the oxide coatings by the argon mixture, due to the ionic doping effect, some argon ions remain in the film layer. Although such argon does not provide any advantage to the film, it could cause many microscopic defects to the film band in lowering the laser-induced damage threshold value. As the ionic energy and current density go up, the doped argon layer also gets bigger to further lower the laser-induced damage threshold value.

4. CONCLUSION

This paper made a study of the ion-assisted deposition techniques, especially the effects of parameters, such as the ion species, ion energy, and ion current density, and on the optical properties of TiO_2, ZrO_2 and SiO_2, such as the film refractive indices, absorption, and laser-induced damage threshold values. Under the same current density, the refractive indices of TiO_2 and ZrO_2 films become larger as the ion energy increases until the ion energy reaches a certain critical value, at which the refractive indices reach their maximum values. However, after the ion energy goes beyond the critical value, the refractive index drops off rapidly. As the ion current density becomes bigger, the critical value of the ion energy becomes smaller. The ion current density has also a similar critical value. Various ion species have different critical values.

The ion species have effects on the absorption characteristics of TiO_2 and ZrO_2 films, and by use of the ion current of a high concentration of oxygen, one can lower the absorption coefficient. It is clear that under the same working conditions, the ion-assisted deposition technique can raise the laser-induced damage threshold values.

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