Fabrication of SiO₂-TiO₂ Double Layers Anti-Reflection Coating by Sol-Gel Method and Study of its Optical Properties

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ABSTRACT. An inexpensive and easily adaptable to industry scale method is Sol-Gel used to get a double layer anti-reflection coating thin film from SiO₂/TiO₂ by dip coating technique and we found that the Q H thickness SiO₂/TiO₂ Double layer thin film gets the best results so, we get a reflectance 0.002-0.02 for ultraviolet region, 0-0.04 for visible region, and 0.004-0.04 for Near infra-red region, and it is better than a thin film from SiO₂ mono layer or thin film from TiO₂ mono layer individually.

1. INTRODUCTION

Coatings have been applied on glass to obtain a glass with more useful properties, such as anti- reflection(AR),anti-static, defogging, anti-abrasion, self-cleaning (SC), solar control and electrical conductivity. compounds are coated as a thin film on glass by a variety of techniques [1–2]. SiO₂ coatings, for example, have attracted attention due to their transmittance of glass as a result of their low refractive index and low surface scattering [3–4]. SiO₂- coated anti-reflective glasses are currently used commercially in TV screens, picture framing, optical lenses and solar panels [5–6]. TiO₂ coatings, have attracted attention in many uses such as in photo voltaic and electro chromic applications[7].

Sol-Gel method is inexpensive and easily adaptable to industry scale and mass production comparing with other physical and chemical vapor methods,. It is possible to work in normal atmospheric conditions and get high homogeneity of the final coatings. The process can be controlled by temperature or through the chemical contents and their molar ratios. There are a variety of options for depositing the coatings, called dip-coating, spin coating, or spray coating on the substrate with the sol.

2. EXPERIMENTAL

2.1. Substrate and cleaning procedure [8]:

We used glass substrates Soda-lime that has 13% Na₂O which dissolved in water and converting to NaOH as a thin film making a collapse in preparing procedure so we can etch this film by washing the substrate with distilled water and apply the cleaning procedure as follows:

1. Put the substrate in 3% solution of normal detergent ultrasonically 5-7 min.
2. Immerse it in HCl 2M for 15 min
3. Washed with distilled water for 20 min
4. Dry it by hot air for 5 min

2.2. Dip coating Sol-Gel Method and Thickness Measurements:

We immersed the cleaned substrate into the Sol and get it up with a controlled with- drawal speed thus, the thickness is related with withdrawal speed and we can calculate it from modified landau – levich equation [8]:

$$h = \frac{0.94 \cdot \eta^{\frac{2}{3}} \cdot v^{\frac{4}{3}}}{\gamma_{LV}^{\frac{1}{6}} (\rho \cdot g)^{\frac{1}{2}}}$$

where: h is the thickness; v is withdrawal speed; η viscosity ; ρ is density; γ is surface tension between vapor and liquid; and g is the gravity acceleration

As we know that to get a best anti reflection coating we have to put double layer where this equation is incontestable:

$$n_1 \cdot n_s = n_0 \cdot n_2$$

where : n_1 is refractive index for the upper layer SiO_2 ($n_1=1.51$)

n_2 is refractive index for the inner layer TiO_2 ($n_2=2.25$)

n_s is refractive index for the soda-lime substrate ($n_s=1.5$)

n_0 is refractive index for the medium ($n_0=1.00$)

So, we make three types of double layer anti reflection coating to use it in the seberal range of the spectrum the first for Ultra Violet (250- 400 nm) and we choose $\lambda=300$ nm is the center wavelength, the second for Visible region (400- 800 nm) and we choose $\lambda=550$ nm is the center wavelength, the third for Near Infra-red region (800- 1200 nm) and we choose $\lambda=1050$ nm is the center wavelength

From each type we make three films depending on its optical thickness; where optical thickness calculated from the equation:

$$h = \frac{k \cdot \lambda}{4n}$$

where: $k=1,2,3,4,\dots$; λ is the center wavelength; n:refractive index

So, when $k=1$ that we get a quarters' thickness film

$k=2$ that we get a half thickness film

$k=3$ that we get a three quarters' thickness film and so on...

Table 1. A data of preparation thicknesses depends on their refractive indices and center wavelength

Film Type	Thickness (nm)	Ultra Violet region	Visible region	Near Infra-red region
		$\lambda=300$ nm	$\lambda=550$ nm	$\lambda=1050$ nm
Quarter-Quarter (Q-Q)	SiO_2	50	92	175
	TiO_2	34	61	117
Quarter- Half (Q-H)	SiO_2	50	92	175
	TiO_2	67	122	234
Quarter-three Quarter (Q-3Q)	SiO_2	50	92	175
	TiO_2	100	183	350

To get a desire thickness probably we have to repeat the procedure of precipitation more than one time or we apply the application one time with different withdrawal speed as it shown in table .2

Table 2. Withdrawal speed for each film SiO₂ or TiO₂

Film type	Thickness (nm)	Withdrawal speed (cm/min)
SiO ₂	50	10.57
SiO ₂	92	16.71
SiO ₂	175	27.06
TiO ₂	34	9.32
TiO ₂	67	15.5
TiO ₂	100	20.93
TiO ₂	61	14.45
TiO ₂	122	24.3
TiO ₂	183	32.9
TiO ₂	117	23.55
TiO ₂	234	39.6
TiO ₂	350	53.57

2.3. Experimental procedure[9-11]:

The TiO₂ sol was prepared in two steps using titanium (IV) butoxide (Ti[O(CH₂)₃CH₃]₄, [Aldrich]. In the first step, ethanol (EtOH) [99.9%] and acetic acid (CH₃COOH) [Merck] were mixed at room temperature for 30 min under the molar ratios TIVBT :EtOH:CH₃COOH=1:100:0.5. In the second step, ethanol was added to the solution so that the molar ratios became TIVBT:EtOH:CH₃COOH=1:150:0.5, After this, the solution was stirred for 1 h more still at room temperature then the solution came out homogeneous and transparent.[12-13]

We prepare thin films from TiO₂ by immersing the cleaned substrate into the Sol and get it up with a controlled withdrawal speed then we put it in the furnace at 100 °C for 15 min, annealed it at 500 °C for 1 hour then we cooled it to room temperature which we called procedure No.1[14-16]

The SiO₂ sol was prepared by tetra ethyl ortho silicate (Si(OC₂H₅)₄, TEOS) [Merck]. TEOS was mixed with isopropanol (C₃H₈O) [Merck] as solvent, distilled water (H₂O) for hydrolysis and hydrochloric acid (HCl) [38% Merck] as catalyst at 70°C for 80 min. The molar ratios were TEOS:C₃H₈O:H₂O:HCl=1:32:32:0.24. the solution was stirred for 1 h more still at room temperature then the solution came out homogeneous and transparent[18-19].

We prepare thin films from SiO₂ by immersing the cleaned substrate into the Sol and get it up with a controlled withdrawal speed then we put it in the furnace at 100 °C for 15 min ,annealed it at 450 °C for 1 hour then we cooled it to room temperature, which we called procedure No.2 [20]

Now we get a cleaned substrate by cleaning procedure and apply first procedure No.1 then the procedure No.2 to get a Double Layer Anti- Reflection Coating to study its optical properties

3. RESULTS AND DISCUSSION

We measure the transmittance and the reflectance and calculate the absorbance for the prepared film with three types (Q Q, Q H , Q 3Q) and get the follows:

Figure 1. Optical properties for Q Q in the whole studied wavelength regions

Figure 2. Optical Properties for Q H in the whole studied wavelength regions

Figure 3. Optical Properties for Q 3Q in the whole studied wavelength regions

As we see the film gets a high transmission upper than 95-99% and low reflection in the whole studied spectrum.

Then we compared our film with theoretical mathematical data for double layer anti-reflection coating in visible region and get the result as follows:

Figure 4. Comparison of the reflectance for Q Q in Visible region (Double Layer Anti-Reflection Coating) theoretical & Practical results

Figure 5. Comparison of the reflectance for Q H in Visible region (Double Layer Anti-Reflection Coating) theoretical & Practical results

Figure 6. Comparison of the reflectance for Q 3Q in Visible region (Double Layer Anti-Reflection Coating) theoretical & Practical results

We found that there is a good match between theoretical and practical results.

Then we study the reflection for each group (region in the studied spectrum) and the results were:

1- Ultra Violet region:

We measure the reflectance for the first group (Double Layer Anti-Reflection Coating) which will be used for the ultra-violet region and we get:

Figure 7. The reflectance for the first group (Double Layer Anti-Reflection Coating) which will be used for the ultra-violet region

We can see that the best film for $\text{SiO}_2/\text{TiO}_2$ (Q H) Double Layer Anti-Reflection Coating for the ultra-violet region

2- Visible region:

We measure the reflectance for the second group (Double Layer Anti-Reflection Coating) which will be used for the Visible region and we get:

Figure 8. The reflectance for the Second group (Double Layer Anti-Reflection Coating) which will be used for the Visible region

We can see that the best film for $\text{SiO}_2/\text{TiO}_2$ (Q H) Double Layer Anti-Reflection Coating for the visible region.

3- Near Infra-red region:

We measure the reflectance for the third group (Double Layer Anti-Reflection Coating) which will be used for the Near Infra-red region and we get:

Figure 9. The reflectance for the third group (Double Layer Anti-Reflection Coating) which will be used for the Near Infra-red region

We can see that the best film for $\text{SiO}_2/\text{TiO}_2$ (Q H) Double Layer Anti-Reflection Coating for the Near Infra-red region.

As a result, we see that is the film $\text{SiO}_2/\text{TiO}_2$ (Q H) is the best for our aims.

Finally, we study the reflectance for double layer $\text{SiO}_2/\text{TiO}_2$ (Q H) as a comparison with a glass, Q thickness SiO_2 mono layer, H thickness TiO_2 mono layer and we get the follows:

Figure 10. Comparison of reflectance for Glass, Q thickness SiO_2 mono layer, H thickness TiO_2 mono layer, Q H thickness $\text{SiO}_2/\text{TiO}_2$ Double layer in Visible region

As we see that the Q H thickness $\text{SiO}_2/\text{TiO}_2$ Double layer thin film was the best.

4. CONCLUSION

The proposed of this study is to get a double layer anti-reflection coating thin film from $\text{SiO}_2/\text{TiO}_2$ by Sol-Gel as an inexpensive method and easily adaptable to industry scale and mass production comparing with other physical and chemical vapor methods, and we found that the Q H thickness $\text{SiO}_2/\text{TiO}_2$ Double layer thin film gets the best results, and it is better than a SiO_2 mono layer or TiO_2 mono layer individually .

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