JOURNAL OF MATERIALS SCIENCE **40** (2005) 1363–1366

Antireflecting coating from Ta_2O_5 and SiO_2 multilayer films

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Sol-gel method is important for depositing antireflective coating that allows control over thickness as well as the index of refraction. Antireflective coatings which are produced from Ta_2O_5 and SiO_2 multi-layer thin films using sol-gel spin coating method are presented. The refractive index and the thickness are controlled by the composition and the concentration of the solution respectively. The thickness, refractive index and extinction coefficient of the films were calculated through transmission and reflection measurement by an NKD analyser. Mechanical properties of the films were checked by the cross tape test and dry sun test at 760 W/m^2. The result shows that the sample heat treated at 450°C for 15 min approaches a reflectance with less than 0.5% at around 840 nm.

1. Introduction

Antireflecting (AR) filters are important for both technical and industrial applications [1]. Antireflective coatings for photovoltaic use are also well known [2–4]. Multilayer coatings are necessary to produce AR systems [5]. Several thin film deposition techniques such as thermal oxide growth, vacuum sputtering, chemical vapour deposition (CVD), plasma enhanced CVD and sol-gel methods [6–9] can be used to produce the multilayer stacks. Most of these methods allow the production of high quality interference filters but the production costs are relatively high. Among these, sol-gel method has some advantages because of low production costs and control over thickness and index of refraction.

In this work we present the result of AR coatings which are produced from Ta_2O_5 and SiO_2 multi-layer thin films using sol-gel spin coating method. A theoretical calculation is also made for the reflectance using transfer matrix method.

The refractive index and the thickness are controlled by the composition and the concentration of the solution respectively. The thickness and refractive index of the films were calculated through transmission and reflection measurement by an refractive index, extinction coefficient and thickness measuring system (NKD analyser, Aquila Instruments). Atomic force microscope (Shimadzu, SPM-9500J3) is used for the surface analysis. Mechanical properties of the films were checked by the cross tape test (ELCOMER 107 Cross-Hutch Cutter) and dry sun test at 760 W/m^2.

2. Theory

The theory of the multilayer film is based on the transfer matrix method [10, 11]. The theory uses the total electric and magnetic fields and their boundary conditions. Each layer of the system is described by a 2 × 2 matrix which contains information on thickness, refractive index and the angle of propagation. The AR systems consist of a glass substrate coated on both sides with three same sequences of layers. If the system consists of three layers and the thicknesses of the layers are equal to quarter wave thickness at a specific wavelength, the minimum reflection from the coated surface for the normal light is given by

$$R = \left(\frac{n_0 n_s n_2^2 - (n_1 n_3)^2}{n_0 n_s n_2^2 + (n_1 n_3)^2}\right)^2 \tag{1}$$

The condition for the anti-reflecting light to be zero is

$$\frac{n_1 n_3}{n_2} = \sqrt{n_0 n_s} \tag{2}$$

where n_1, n_2, n_3 are the refractive indices of the layers and n_0, n_s are the refractive index of air and the substrate, respectively. We did not take absorption into account since the glass and the films at the wavelength region that we are interested have nearly zero absorption.

Following consideration is made to find total reflectance of the double sided AR system: The total

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thickness of the multilayer films on side1 and side2 are around 500 nm which is the same order as the wavelength of the incident light. Therefore, the multiply reflected and transmitted beams as the light passes through the films were considered to be coherent. On the other hand the thickness of the substrate is around 10^6 nm, so beams whose path difference involves one or more traversals will be assumed as incoherent. The reflection and transmission coefficients r_1, t_1 for a beam passing through the multilayer stack from outside in and r_2, t_2 from inside out are determined by the standard transfer matrix method [10, 11]. The reflection and transmission coefficients for beams making multiple passes through the substrate are just products of r_1, r_2, t_1 and t_2. To find the total R, we sum the coefficients of the series of the beams incoherently.

$$R = |r_1|^2 + \sum_{n=0}^{\infty} \left| t_1 r_2^{2n+1} t_2 \right|^2 = |r_1|^2 + \frac{|t_1 r_2 t_2|^2}{1 - |r_2|^4} \quad (3)$$

We thus can calculate R given the thicknesses and refractive indices of the layers.

3. Experimental procedure

3.1. Sol preparation for the AR filters

Preparation of the Ta_2O_5 is described elsewhere [12]. SiO_2 coating solutions were prepared by dissolving 5.35 ml of TEOS ($Si(OC_2H_5)_4$) in 10.6 ml of ethanol by stirring for 30 min. Second solution is obtained by stirring 6.76 ml of distilled water, 10.6 ml of ethanol and 0.96 ml of HCl for 30 min. The second solution is added to the first solution slowly and stirred for 30 min.

3.2. Coating process for the AR filters

Since the refractive index and thickness are important parameters for the suitable AR materials, the composition of the solution is determined by the index requirement. The thickness of the coating is controlled by the concentration of the solution as well as the spin rate. Corning 2947 were used as substrates.

Various proportion of Ta_2O_5-SiO_2 mixtures are used to reach the desired refractive index and thickness values. Figs 1 and 2 show the refractive indices of these mixtures with respect to Ta_2O_5 proportion in SiO_2 at 550 nm for the films heat treated at 100 and 450°C, respectively. Figs 3 and 4 show the thickness of these mixtures with respect to Ta_2O_5 proportion in SiO_2 for the films heat treated at 100 and 450°C, respectively. The conditions for the antireflecting light to be near to zero are estimated by theoretical calculation using suitable thickness and index values from our composition graphs.

Two double sided systems were made. They are designed such a way that n_3, n_2 and n_1 was the first, second and third layer respectively on both sides of the substrate. In the System I, layer3 (n_3) was coated with 60% Ta_2O_5–40% SiO_2 mixture, layer2 (n_2) was made from Ta_2O_5, and layer1 (n_1) was made from 10% Ta_2O_5–90% SiO_2 mixture. Each layer was heat treated at 100°C for 5 min.

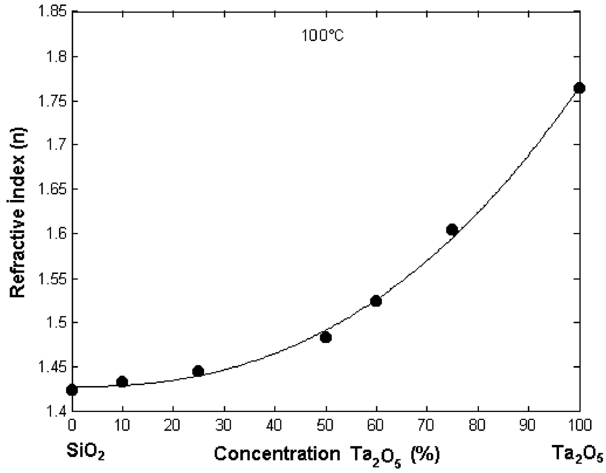


Figure 1 Refractive index vs. Ta_2O_5 proportions in SiO_2 at 550 nm which are prepared at 100°C.

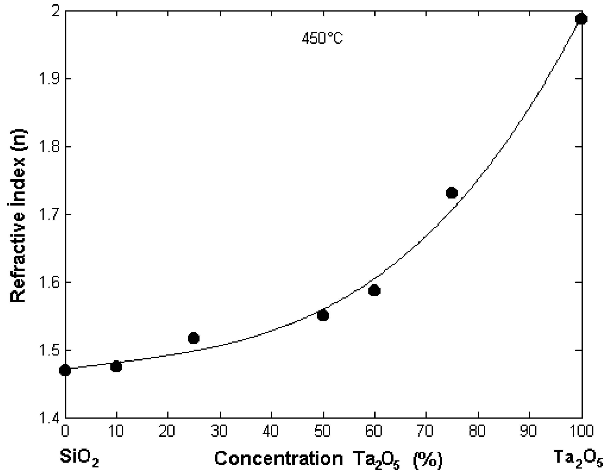


Figure 2 Refractive index vs. Ta_2O_5 proportions in SiO_2 at 550 nm which are prepared at 450°C.

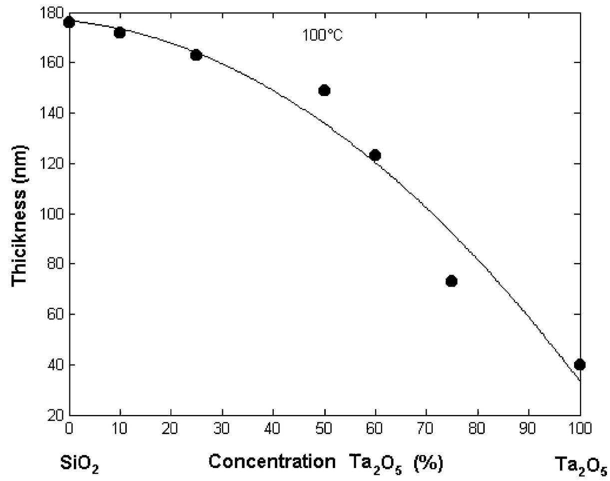


Figure 3 Thickness vs. Ta_2O_5 proportions in SiO_2 which are prepared at 100°C.

In the System II, layer3 (n_3) was coated with 75% Ta_2O_5–25% SiO_2 mixture, layer2 (n_2) was made from Ta_2O_5 and layer1 (n_1) was made from 10% Ta_2O_5–90% SiO_2 mixture. Each layer was heat treated at 100°C for 5 min and the final system was heat treated at 450° for 15 min.

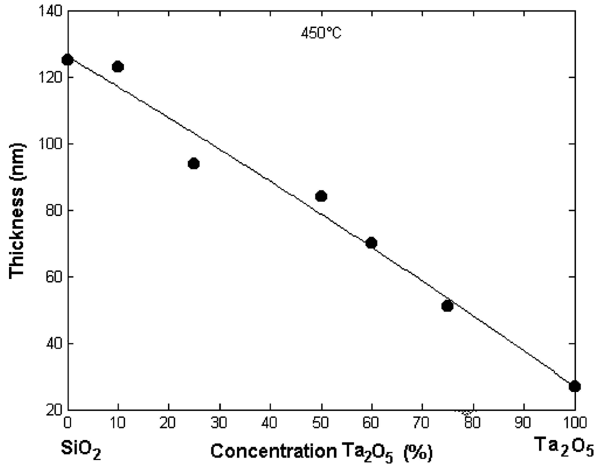


Figure 4 Thickness vs. Ta_2O_5 proportions in SiO_2 which are prepared at 450°C.

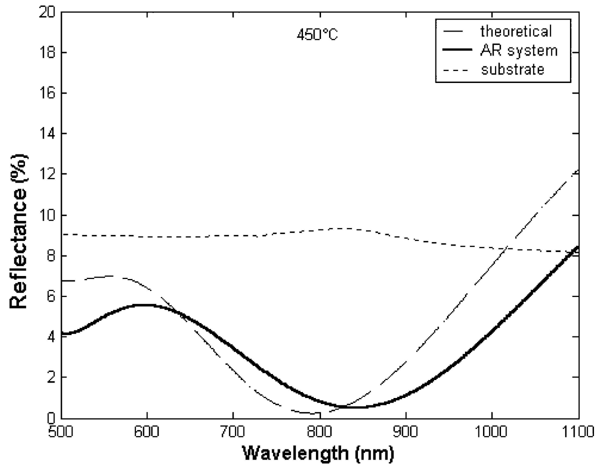


Figure 6 Refractive index vs. wavelength for the three layer antireflective system prepared at 450°C heat treatment.

3.3. Characterization of AR coatings

An NKD-7000V system is used to evaluate transmission and reflection of AR filters at the incident angle of 30°. The single layer thickness and refractive indices were determined with the Pro-Optix package program included in the NKD system. A spectrophotometer (Jasco V-530, Shimadzu) is used to obtain the reflectance of the AR system at the normal incidence. The adhesion of the coatings was tested by cross cut and tape test. The films were irradiated at 765 W/m^2 for 24 h for the dry sun test.

4. Results and discussion

Fig. 5 shows the experimental and theoretical reflectance of the AR system for the normal incident light. The films are heat treated at 100°C for 5 min after each coating. The figure shows 0.6% reflectance at around 900 nm. The systems reflectance is below 1% in between 850–950 nm and below 2% in between 815–995 nm. The discrepancies between the experimental data and theoretical values are due to the thickness and refractive index variation which we used the values obtained from single layer measurement. The films are heat treated several times when the multilayer AR system was constructed. This reduces the thickness of the film as the residuals from sol-gel synthesis are removed from the film.

Fig. 6 shows the experimental and theoretical reflectance of the AR system for the normal incident light. The films are heat treated at 100°C for 5 min after each coating. The final system was heat treated at 450°C for 15 min. The figure shows 0.5% reflectance at around 840 nm. The systems reflectance is below 1% in between 790–895 nm and below 2% in between 750–935 nm. Similar reason may be given for the

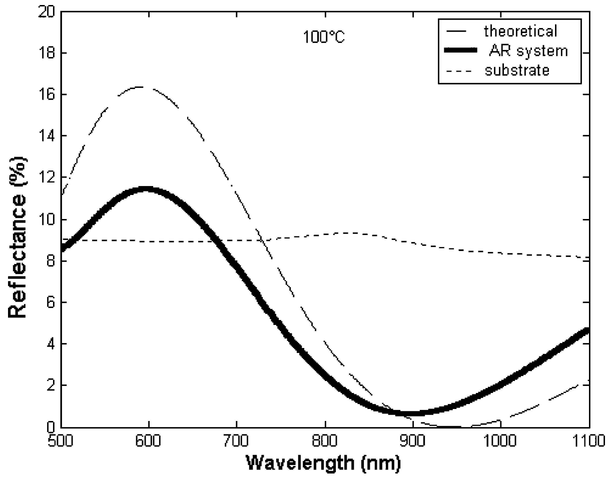
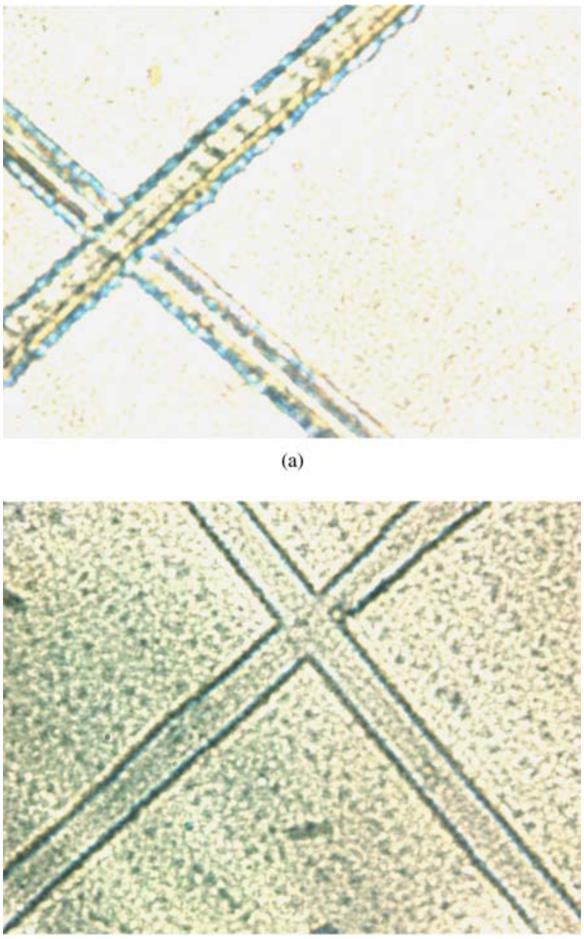


Figure 5 Refractive index vs. wavelength for the three layer antireflective system prepared at 100°C heat treatment.



(a)

(b)

Figure 7 Cross hutch cutter test results of the samples prepared at (a) 100°C and (b) 450°C.

TABLE I The calculated values of the refractive indices at 550 nm and thicknesses of the first and second system

	Material	Thickness (nm)	Refractive index	Number of layers
System I	10% Ta_2O_5–90% SiO_2	172	1.43	1
	Ta_2O_5	122	1.76	3
	60% Ta_2O_5–40% SiO_2	123	1.51	1
System II	75% Ta_2O_5–25% SiO_2	123	1.46	1
	Ta_2O_5	108	1.95	4
	10% Ta_2O_5–90% SiO_2	51	1.71	1

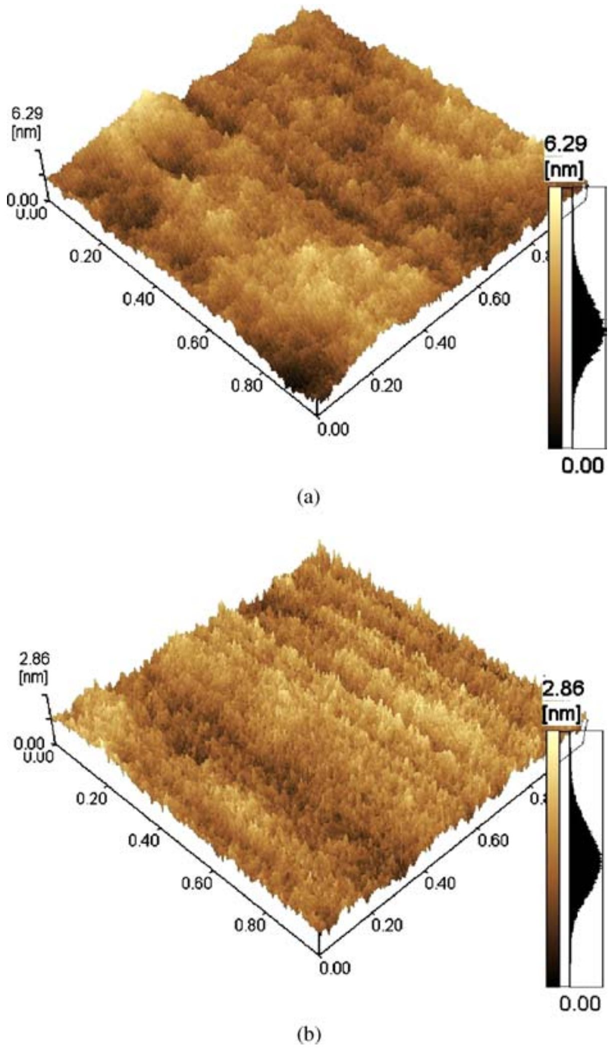


Figure 8 AFM images of the AR films prepared at (a) 100°C and (b) 450°C.

discrepancies between the theoretical and experimental values as explained above.

The calculated values of the refractive indices at 550 nm and thicknesses of the first and second system are given in Table I. The values are calculated from the Pro-Optix software in the NKD system.

Fig. 7 shows that both systems had very good adhesion under the cross-cut and tape test (5B [13]). The films also have very smooth surface (Fig. 8(a) and (b)) with average roughness of around 6 and 3 nm. Dry sun test at 765 W/m^2 shows no observable intensity change.

5. Conclusion

Antireflective filters have been prepared by the sol-gel dip coating method. The results showed that Ta_2O_5 and SiO_2 are suitable materials to develop such type of filters especially for the near infrared region. The variation in the index of refraction and the thickness with the mixture percentage of Ta_2O_5–SiO_2 solution give some flexibility on choosing the center of antireflective region. The sol-gel derived AR coatings also exhibit homogeneity of the surfaces and good adhesion properties.

Acknowledgements

The authors would like to acknowledge Esat Pehlivan for his computational support and Dursen S. Hinczewski for her assistance in helpful discussions. This study was supported by the Turkish State Planning Organization.

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