

SOL-GEL DERIVED ANTIREFLECTIVE COATINGS FOR SILICON*

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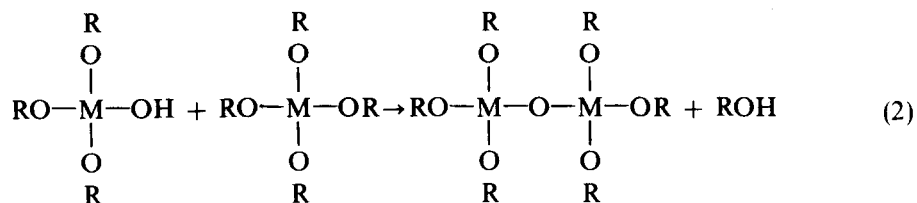
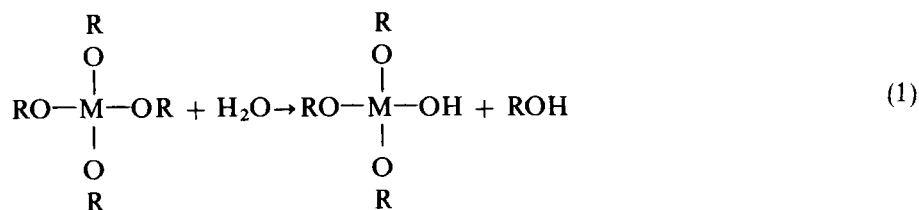
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TiO₂-SiO₂ films containing from 30 to 95 mol% TiO₂ were prepared by a sol-gel process. These films were applied to polished silicon and heat treated at temperatures less than 450°C to convert the applied films to amorphous oxide films ranging in refractive index from approximately 1.63 to 2.17. The films were evaluated for antireflectance as a function of conversion temperature. It was found that the sol-gel films applied at 400°C showed broad regions of antireflectance compared to other titanium-based films.

1. Introduction

Recently, it has been shown that thin, optical quality amorphous films can be applied to a variety of substrates by sol-gel processes [1-3]. These processes utilize metal alkoxides of network forming cations as glass precursors. The alkoxides are polymerized at low temperatures in alcoholic solutions to form glass-like networks linked by bridging oxygens as shown by the following reaction sequence:



In reaction (1), the metal alkoxide, M(OR)₄, (R ≡ C_xH_(2x+1)⁻¹) is partially hydrolyzed to form a soluble polymerizable specie which may undergo self-condensation

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to form a bridging oxygen plus an alcohol as shown in (2). The resulting dimer remains soluble in alcohol as long as some OR groups are retained [4] and is capable of further polymerization to form a larger molecular specie. Dilute solutions containing these polymerized species can be used to coat both ceramic and metal substrates by conventional dipping, spinning or spraying operations. The applied coating is converted to a dense glass coating by heat treatments less than the glass softening point temperature.

Reflectivity from a coated surface is given by Fresnel's equation

$$R = \left(\frac{n_c^2 - n_1 n_2}{n_c^2 + n_1 n_2} \right)^2, \quad (3)$$

where n_c , n_1 and n_2 are the refractive indices of the coating, the environmental medium and the substrate, respectively. If the reflectivity is minimized for a particular wavelength, λ_0 , the refractive index and thickness of the coating must satisfy the conditions

$$n_c = (n_1 n_2)^{1/2} \quad (4)$$

$$t_c = \lambda_0 / 4n_c, \quad (5)$$

respectively. According to these relations, the optimum coating index and thickness for silicon substrates are $n_c \approx 2.0$ and $t_c \approx 725 \text{ \AA}$ for $\lambda_0 = 580 \text{ nm}$. For silicon solar cells λ_{min} is usually chosen equal to or very near 600 nm [2].

To achieve the high refractive index necessary for forming an antireflective film for silicon, SiO_2 doped TiO_2 , Ta_2O_5 and SiN_x [5] have generally been applied by vacuum sputtering, plasma, or chemical vapor deposition methods which are estimated to cost \$0.20/W package. Recently, Yoldas applied TiO_2 - SiO_2 films by a sol-gel process which was estimated to cost only \$0.01/W package.

There have been several reports of the properties of gel-derived TiO_2 - SiO_2 glasses [1, 4]. However, to date, there has been no description of the sol-gel process employed. The purposes of this investigation were to establish a particular procedure for preparing TiO_2 and TiO_2 - SiO_2 glass films and to evaluate these films as AR coatings for silicon as a function of both composition and heat treatment temperature. In order to make the coatings compatible with most solar cell fabrication processes, it is desirable to minimize the film cure temperature. Therefore, a goal of this investigation was to produce AR coatings at or below 400°C . The film properties obtained were compared to those previously obtained in investigations where the specific preparation methods were not revealed.

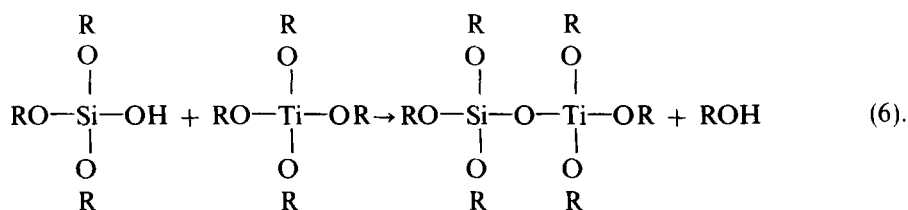
2. Experimental

2.1. Solution preparation

Titanium tetraethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) and silicon tetraethoxide ($\text{Si}(\text{OC}_2\text{H}_5)_4$) were used as precursors of TiO_2 and SiO_2 . These alkoxides which are mutually

soluble in ethanol both hydrolyze according to (1) but at different rates. Because Ti $(OC_2H_5)_4$ hydrolyzes rapidly compared to $Si(OC_2H_5)_4$, water cannot be directly added to a mixture of the alkoxides without preferential and complete hydrolysis of $Ti(OC_2H_5)_4$ to form the precipitate, $Ti(OH)_4$. Therefore, the preparation technique involves the separate partial hydrolysis of one or both alkoxides prior to their mixing [4].

Solutions containing up to 50% TiO_2 can be made by adding $Ti(OC_2H_5)_4$ to a solution containing partially hydrolyzed silicon tetraethoxide as described by Yoldas [4]. Self-condensation reactions (2) occur slowly compared to the condensation reactions which form Si-O-Ti bonds according to:



Therefore, dissimilar constituents tend to become neighbors [4] and the solution becomes homogeneous on a molecular level.

When the required Ti/Si ratio was greater than 1, both ethoxides were partially hydrolyzed before mixing. Titanium ethoxide was added to ethanol which contained 1 vol% HNO_3 (70%). A requisite amount of water was added to achieve a molar ratio $H_2O/Ti(OC_2H_5)_4$ of 1:1. After addition of water, the solution pH was ≈ 2 . At these low (OH) concentrations, hydrolysis occurs slowly without precipitation. The partially hydrolyzed Si and Ti solutions were mixed volumetrically to obtain specific Ti/Si ratios. The exact procedure for the preparation of a 90% TiO_2 10% SiO_2 solution is shown schematically below. This procedure resulted in a solution containing an equivalent oxide content of 4.9 wt%.

Ti solution	Si solution
combine at 25°C	combine at 25°C
1000 ml C_2H_5OH	100 ml EtOH
10 ml HNO_3 (70%)	100 ml $Si(OC_2H_5)_4$
100 ml $Ti(OC_2H_5)_4$	8.2 ml H_2O
heat to 40°C and add	heat to 60°C
8.6 ml H_2O	stir for 30 min
stir for 30 min	

Combine in a volume ratio 47.5 (Ti):1(Si) at 40°C, stir for 30 min

A total of six compositions were used in this investigation ranging from 95% TiO_2 5% SiO_2 to 10% TiO_2 90% SiO_2 . Specific compositions are listed in table 1.

Table 1
Compositions investigated in mol%,

	TiO ₂ (mol%,)	SiO ₂ (mol%,)
ST 1	95	5
2	90	10
3	70	30
4	50	50
5	30	70
6	10	90

2.2. Sample preparation

Solutions were applied to polished, circular (1 and 2" diameter) silicon wafers by a spinning process. Equal amounts of solutions (18 drops) were added dropwise to wafers spinning at a constant RPM (4500 RPM unless otherwise noted). Specimens were spun for 45 s after the final solution addition and dried under a heat lamp for a minimum of 10 min. Coated wafers were successively heated in air at each of the following temperatures: 200, 300, 350, 400 and 450°C. At each temperature the samples were inserted into a temperature stabilized furnace and held for a period of 15 min and withdrawn. Optical measurements were performed after each heat treatment.

2.3. Optical measurements

Reflectivity was measured continuously from 300 to 800 nm on a Beckman model UV 5240 spectrophotometer using a "Halon" sample plate as the 100% reflectance standard.

Film thickness and refractive index were measured on a Gaertner model L119-X automated ellipsometer using a helium-neon laser light source ($\lambda=6328 \text{ \AA}$). The incident angle was maintained at 60°.

2.4. Chemical durability

The durability of 95 and 90% TiO₂ coatings was evaluated in both acidic and basic environments. Coated wafers were submerged in 1% solutions of HCl, NH₄OH and NaOH maintained at 23°C and stirred with a magnetic stir bar. Reflectivity, thickness and refractive index were measured as a function of exposure time.

3. Results

3.1. Refractive index and coating thickness

Coating refractive indices were found to increase linearly with titanium content as

shown in fig. 1. Refractive index also increased with heat treatment temperature for each composition as a result of film densification. Therefore a particular range of refractive indices could, in general, be obtained either by varying temperature for a given composition or by varying composition for a given temperature. The refractive index obtained at 400°C for each composition (fig. 1) corresponded well to an additive mixture of SiO₂ and TiO₂. However, at this low temperature the extrapolated value for pure SiO₂ was only 97% of theoretical (1.45) and that of TiO₂ only 93% of the value reported by Yoldas [1, 4] for vacuum baked titania films (2.4). Schroeder reported that in this binary full density is generally achieved by higher temperature heat treatments (500–550°C). Values of refractive index obtained by Schroeder (fig. 1) showed a parallel shift toward higher values indicative of higher heat treatment temperatures.

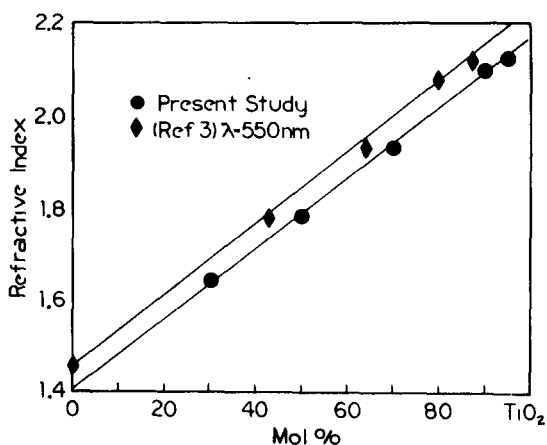


Fig. 1. Refractive index versus mol%, TiO₂ for 400°C specimens (●). Maximum values obtained by Schroeder [3] (◆).

Fig. 2, 3, and 4 show film thickness and refractive index as a function of treatment temperature for the three compositions investigated highest in titanium content. 90 and 95% TiO₂ films attained the desired index, 2.0, at quite low temperatures – 230 and 200°C, respectively. 70% TiO₂ films, however, exhibited a lower index than required by eq. (4) throughout the entire heat treatment range investigated.

Because no combination of composition and temperature satisfied both the calculated thickness and index requirements, spin speed was varied for a particular composition, temperature condition. Fig. 5 shows the effect of spin speed on thickness of 90% TiO₂ films heated to 400°C. Increased spin speeds decreased film thicknesses as reported by Yoldas [1]. Higher speeds had marginally lesser effects. Fig. 5 indicates that spin speeds of 2500–3000 RPM should provide the required coating thickness.

3.2. Reflectivity

Spectral reflectivity was measured as a function of heat treatment temperature.

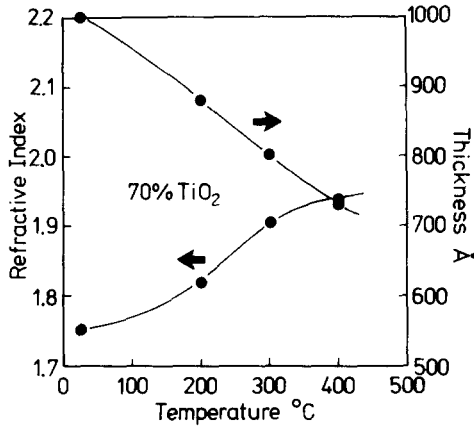


Fig. 2. Refractive index and film thickness versus heat treatment temperature for 70% TiO₂ 30% SiO₂ films.

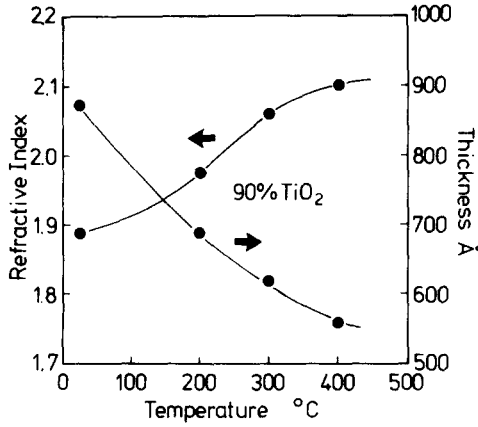


Fig. 3. Refractive index and film thickness versus heat treatment temperature for 90% TiO₂ 10% SiO₂ films.

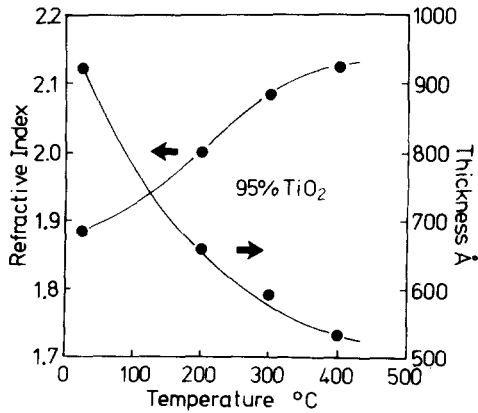


Fig. 4. Refractive index and film thickness versus heat treatment temperature for 95% TiO₂ 5% SiO₂ films.

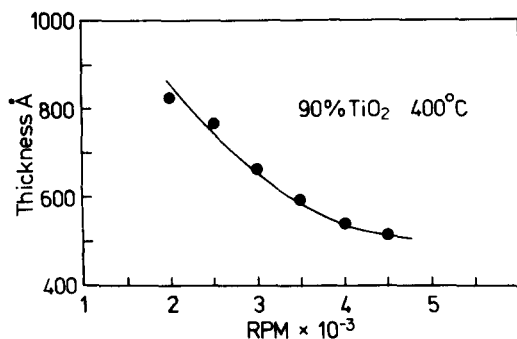


Fig. 5. Film thickness versus spin speed for 90% TiO₂ 10% SiO₂ films fired to 400°C.

Figs. 6 and 7 show the results for 70 and 90% titanium films. For both compositions, λ_0 decreased with heat treatment temperature according to eq. (5) due to the large decrease in film thickness (>30%) compared to the increases in refractive index (<12%). Figs. 6 and 7 indicate that by controlling film thickness comparable spectral reflectivity can be obtained either by heating 70% TiO₂ films to 450°C or by heating 90% TiO₂ films to only 350°C. Because chemical durability of TiO₂-SiO₂ films increases with both titanium content and bake temperature, there are advantages to

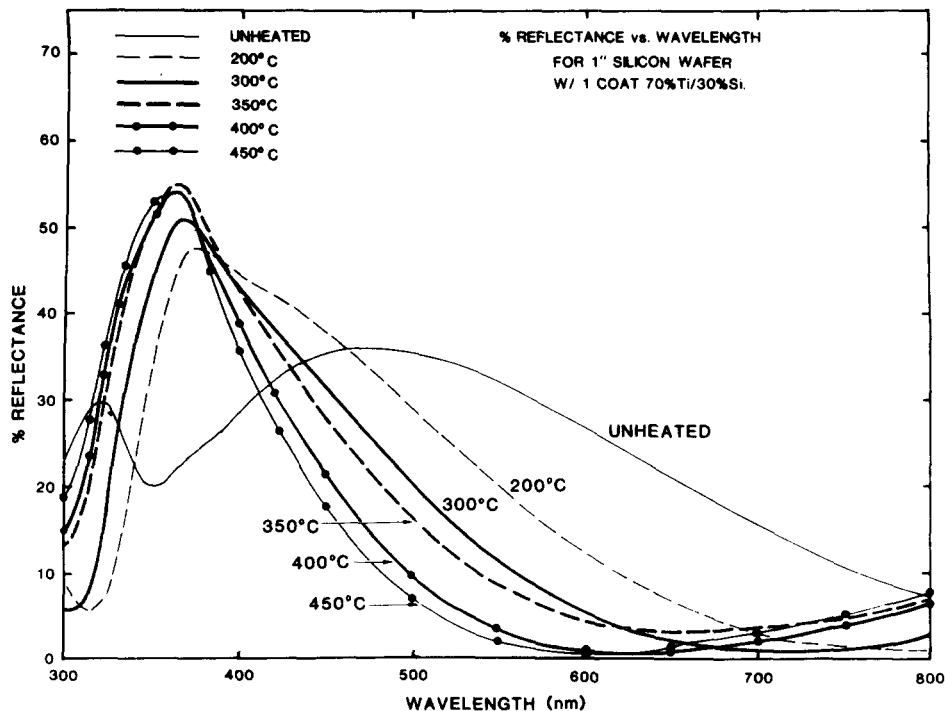


Fig. 6. Spectral reflectance of 70% TiO₂ 30% SiO₂ films as a function of heat treatment temperature.

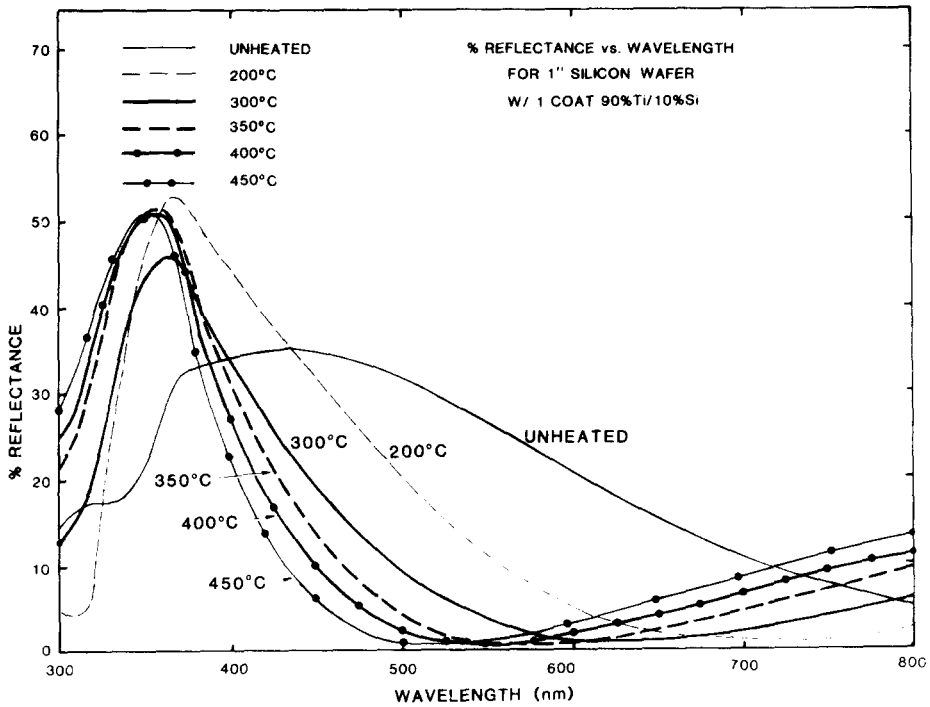


Fig. 7. Spectral reflectance of 90% TiO_2 10% SiO_2 films as a function of heat treatment temperature.

both compositional systems. However, the requirement of low temperature coatings prompted further investigation of the 90% TiO_2 composition.

For a specific composition and heat treatment, reflectivity is minimized by optimizing film thickness. The effect of film thickness for 90% TiO_2 films heated to 400°C is shown in fig. 8. Increased film thicknesses resulted in increased values of λ_0 in accordance with eq. (5). For the refractive index obtained at 400°C, 2.12, eq. (5) predicts $\lambda_0 = 560$ nm for a 660 Å film. This corresponds well to the measured minimum, 570 nm.

For sol-gel applied TiO_2 - SiO_2 films, spectral reflectance can be exactly tailored by adjusting any of the three continuous parameters: composition, film thickness and heat treatment temperature. This results in increased flexibility over single component systems. Spectral reflectance of a 90% TiO_2 film is plotted in fig. 9 and compared with a plasma deposited SiN_x film, [5] a pure TiO_2 film, [2] and an 88% TiO_2 12% SiO_2 film [1]. Because λ_0 can be easily shifted by proper control of film thickness (e.g., fig. 7), the quality of AR coatings prepared by each coating procedure is best judged by comparing the band widths over which good antireflectance is obtained. Such a comparison is shown in table 2 where the spectral width at which reflectance is less than or equal to 5% is listed for each coating procedure referenced in fig. 9. Plasma deposited SiN_x coatings show the broadest region of antireflectance; however, sol-gel applied TiO_2 - SiO_2 films are less expensive to apply than plasma coatings and are potentially hermetic so that the AR coating could serve as an environmentally

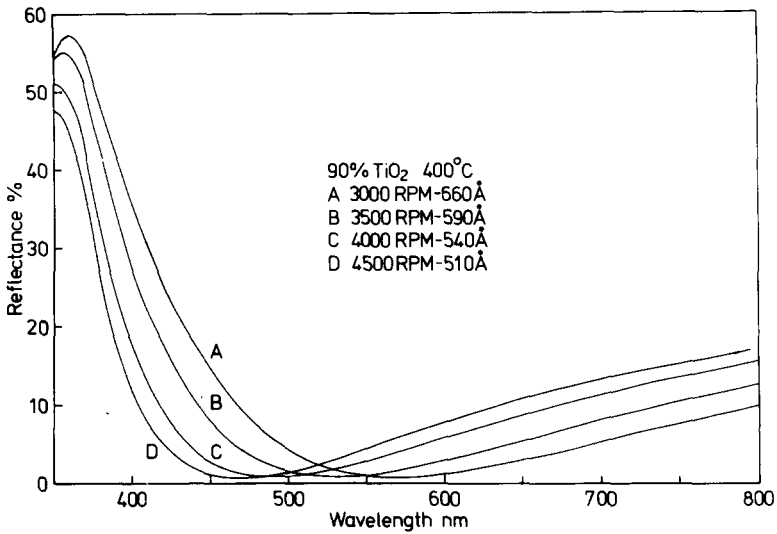


Fig. 8. Spectral reflectance of 90% TiO₂ 10% SiO₂ films fired to 400°C as a function of film thickness.

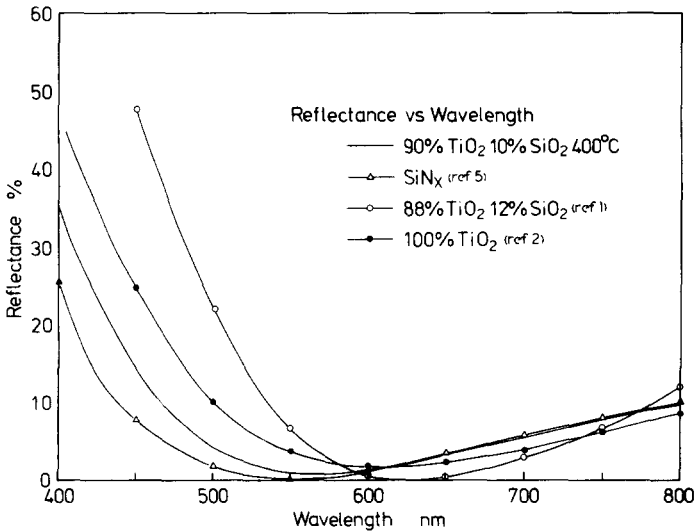


Fig. 9. Spectral reflectance of 90% TiO₂ 10% SiO₂ films fired to 400°C. Shown for comparison are a plasma SiN_x film (680 Å) [5], an 88% TiO₂ 12% SiO₂ film [1], and a 100% TiO₂ film [2].

protective coating as well. The broader region of antireflectance obtained for 90% TiO₂ films fired at 400°C compared with similarly prepared 88% TiO₂ films fired at 450°C [1] suggests that at 400°C the gel films are actually graded in refractive index across their thickness. It is well known that graded index AR coatings exhibit a wider region of antireflectance than single index coatings. This hypothesis may be supported by the fact that for films of the same index, broader regions of antireflectance were

Table 2
Bandwidth at which reflectance is less than or equal to 5%₀
for various antireflective coatings

Coating procedure	Width at which $R \leq 5\%_0$
plasma SiN _x (680 Å, $n = 1.96$)	220 nm
90% TiO ₂ 10% SiO ₂ (660 Å, $n = 2.12$)	196 nm
100% TiO ₂ (670 Å, $n = 2.18$)	180 nm
88% TiO ₂ 12% SiO ₂ (750 Å, $n = 2.0$)	160 nm

obtained for thicker films (fig. 8). As film thickness increased, Schroeder [3] observed decreases in density and refractive index toward the surface which he explained by increased levels of intrinsic stress. This phenomenon should provide good spectral antireflectivity; however, film hardness and chemical durability might be detrimentally affected. For thicker films of the same index, computer modeling of ideal films (i. e. films where $K=0$ and n is constant) predicts broader regions of antireflectance [5]; however, it has not yet been established that sol-gel films behave ideally.

3.3. Chemical durability

The chemical durability of TiO₂ and TiO₂-SiO₂ films has been investigated by several workers. [1-3]. Schroeder [3] found a strong dependence of chemical durability on heat treatment temperature and composition for TiO₂ and TiO₂+SiO₂ films. The logarithm of durability increased linearly with temperature from 200 to 550°C. Pure TiO₂ films were superior to TiO₂+SiO₂ films in both acidic and basic solutions. For TiO₂+SiO₂ films fired to 400°C observable deterioration was observed after 60 h in 10% HCl and after only 10 h in 10% NaOH solutions at room temperature. Yoldas [1] found no observable deterioration for pure TiO₂ films, fired to 500°C in air, after 75 days in 1% HCl at room temperature. Deterioration was obvious, however, after 7 days in 1% NH₄OH solutions. Kern and Tracy [2] found no observable deterioration for pure TiO₂ films fired to 450°C after 1 h at 85°C in 1% solutions of HCl and NH₄OH.

In the present investigation, 90 and 95% TiO₂ coatings applied to polished silicon wafers and heated to 400°C, were immersed in 1% solutions of HCl, NH₄OH and NaOH. Spectral reflectivity, film thickness and refractive index were measured before the immersions and after selected periods of immersion time. The reflectivity results are plotted in figs. 10, 11 and 12. Fig. 10 shows no change occurred in spectral reflectance after a 24 h immersion in HCl, but a major shift toward lower wavelengths was observed after 192 h. The same effect was observed for 90% TiO₂ films. No changes in reflectance were observed after 192 h in 1% NH₄OH (fig. 11). The stronger base, NaOH, caused a small shift in spectral reflectance and visually noticeable deterioration of the film after only 48 h (fig. 12). The corresponding thickness and refractive index measurement results are presented in figs. 13, 14 and 15. 1% HCl (fig. 13) caused no significant changes in thickness for 95% TiO₂ films, but significantly reduced the

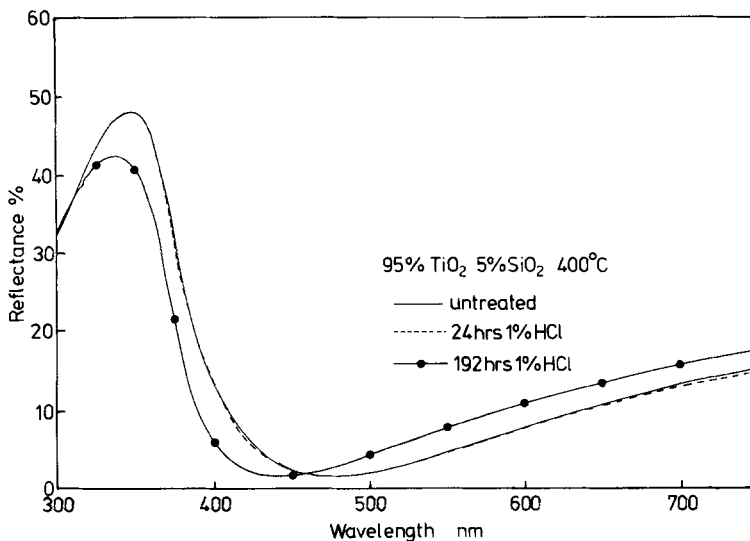


Fig. 10. Spectral reflectance of 95% TiO_2 5% SiO_2 films as a function of immersion time in 1% HCl solutions.

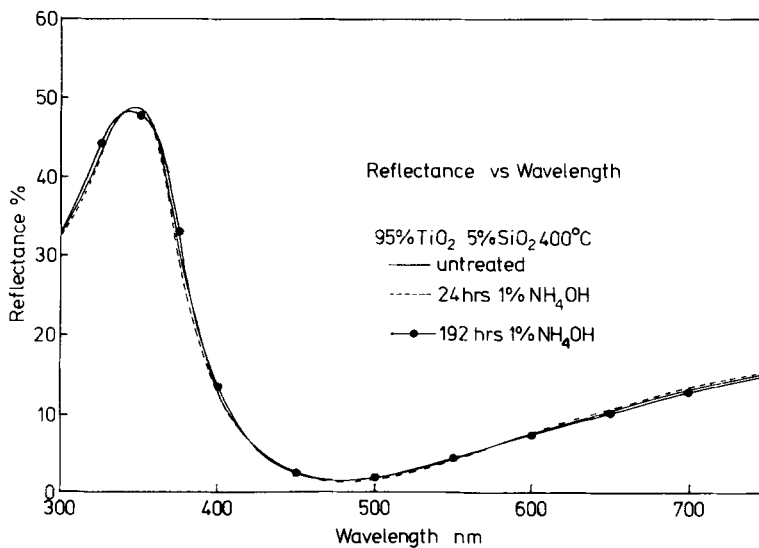


Fig. 11. Spectral reflectance of 95% TiO_2 5% SiO_2 films as a function of immersion time in 1% NH_4OH solutions.

refractive index causing the measured shift in λ_0 to lower wavelengths (fig. 10). 90% TiO_2 films showed a reduction in both thickness and index which resulted in a similar shift in spectral reflectance. 1% NH_4OH solutions caused no significant changes in either thickness or index (fig. 14). 1% NaOH solutions, however, caused a swelling of

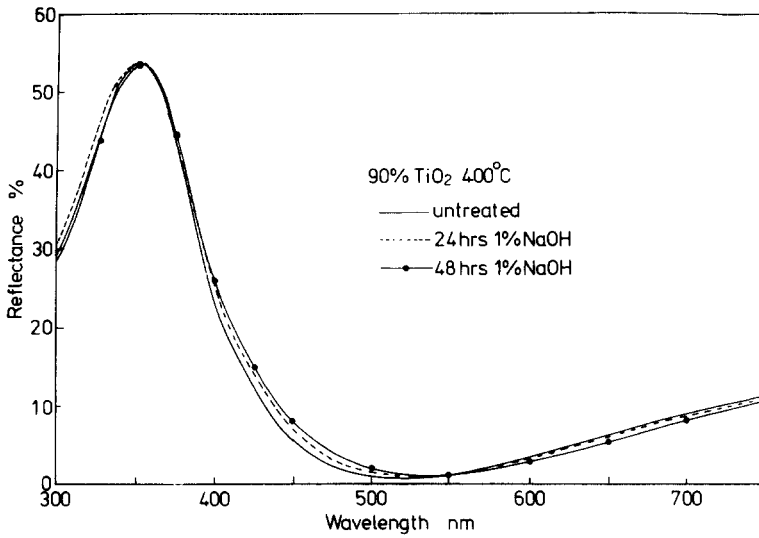


Fig. 12. Spectral reflectance of 90% TiO₂ 10% SiO₂ films as a function of immersion time in 1% NaOH solutions.

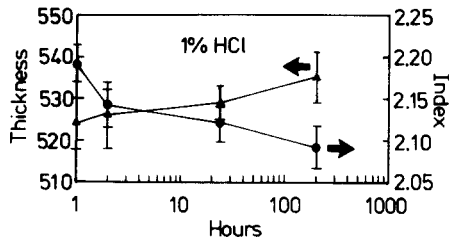


Fig. 13. Film thickness (Å) and refractive index for 95% TiO₂ films as a function of immersion time in 1% HCl solutions. Bars indicate 95% confidence intervals.

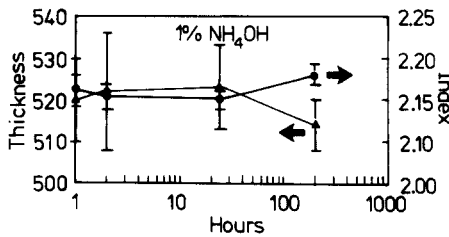


Fig. 14. Film thickness (Å) and refractive index for 95% TiO₂ films as a function of immersion time in 1% NH₄OH solutions. Bars indicate 95% confidence intervals.

the film combined with reduced refractive index. These changes are offsetting with respect to λ_0 and resulted in only a slight positive shift in spectral reflectance (fig. 12).

The results of this investigation indicate the following hierarchy of chemical attack

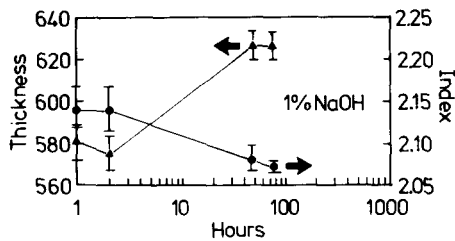


Fig. 15. Film thickness (Å) and refractive index for 90% films as a function of immersion time in 1% NaOH solutions. Bars indicate 95% confidence intervals.

NaOH > HCl > NH₄OH. This is consistent with Schroeder's results for TiO₂ + SiO₂ films immersed in NaOH and HCl solutions, but in conflict with Yoldas' results for TiO₂ films in HCl and NH₄OH. Yoldas, however, found increased resistance to NH₄OH solutions at lower film treatment temperatures where some organics might be retained. SiO₂ additions to TiO₂ films increase the temperature required for complete thermal chemical polymerization of the precursor alkoxides, eq. (2). Pure TiO₂ gels heated to 400°C are completely reacted [4]. However, by 400°C, 90% TiO₂ gel films were only 93% reacted according to weight loss measurements. The retention of some OR groups may have a positive effect on resistance to NH₄OH.

It should be noted that 1% HCl solutions caused no visually observable deterioration of the films other than slight color changes over long periods of time. Observable deterioration was the only chemical durability criterion specified by any of the previous workers [1-3].

4. Conclusions

A relatively simple, sol-gel process was described to prepare TiO₂-SiO₂ AR coatings from alkoxide precursor solutions. 90% TiO₂ 10% SiO₂ coatings heated to 400°C were shown to result in broader band antireflective properties compared to previously investigated TiO₂ based films [1-3]. It is felt that this might result from a graded refractive index. Plasma SiN_x coatings were shown to have superior performance; however, sol-gel TiO₂-SiO₂ coatings are less expensive and are potentially hermetic so that they could also serve as environmentally protective coatings.

Sol-gel AR coatings were optimized by altering any of the three continuous parameters: composition, film thickness or heat treatment temperature. Comparable AR coatings were prepared from 70% TiO₂ films heated to 450°C and 90% TiO₂ films heated to 350°C. Because chemical durability generally increases with TiO₂ content [3], 90% TiO₂ films were considered preferable especially for low application temperatures (400°C).

Chemical durability of 90 and 95% TiO₂ films fired to 400°C was comparable to that reported by other workers [1-3] with the possible exception of HCl attack. Higher heat treatment temperatures should provide increased resistance to acid attack, but such treatments could have detrimental effects on other solar cell components. Longer

heat treatment times or heat treatments in vacuum [1, 4] should be considered to provide increased chemical durability for 400°C films.

References

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