

of the response time can be gathered, Table I. The main point is that the current response of the  $\text{WO}_3$ /polyaniline junction is sluggish. Even at only 1 Hz,  $I_{\text{forward}}/I_{\text{reverse}} = 8.8$ , which is already about 50 times lower than the steady-state rectification factor, indicating a fairly large delay in the discharge of the two materials. Interestingly, even at 1 kHz the devices retain some rectification ability, as is demonstrated by the value of the rectification factor, which is still slightly larger than unity ( $\sim 1.4$ ). While polyaniline switches rapidly between its insulating and conducting states, up to 1 kHz in liquid electrolyte<sup>11</sup> and up to 100 Hz in poly(vinyl alcohol)/ $\text{H}_3\text{PO}_4$  solid electrolyte,<sup>4</sup> the kinetics of  $\text{WO}_3$  redox chemistry are found to be more sluggish. Switching speeds on the order of only several hertz even in aqueous acid<sup>4c</sup> have been reported. Therefore, we attribute the sluggish switching of the diode device to the slow response of  $\text{WO}_3$  and not to the slow response of polyaniline.

### Conclusion

Both  $\text{WO}_3$  and polyaniline have been confined in a controlled manner onto a microelectrode array consisting of eight individually addressable microelectrodes. Both the amount and spatial distribution of the redox materials can be controlled to yield various electrochemical systems yielding characteristics that stem from the properties of the individual components. The redox materials can be placed either separately (to yield transistors or diodes) or in physical contact (to yield diodes) on the microelectrode array. The poly(vinyl alcohol)/ $\text{H}_3\text{PO}_4$  solid-state polymer

electrolyte is used to cover the assembly of derivatized microelectrodes. The switching properties of the resulting "solid-state" devices have been characterized, and a microelectrochemical, solid-state rectifying device based on the interface of  $\text{WO}_3$  with polyaniline has been assembled. Interestingly, the two redox materials do not have to be in physical contact as long as there is a hardwire connection between them. The hardwire connection procedure may be useful in constructing a myriad of diode devices based on redox materials with widely different properties where a good, direct connection between the materials may be difficult to achieve. Additionally, the hardwire approach allows a chip to be reconfigured *after* being derivatized with different redox materials. For example, an array of eight microelectrodes could be functionalized with four redox materials to give four individually addressable transistors or be hardwired to give six different diodes. Obviously, the reconfiguration of diodes having physical junctions would be difficult. However, the maximum number of independently operating diodes on the eight electrode array with hardwire connections is two requiring three redox materials, whereas physical junctions would allow as many as four independently operating diodes using four different materials.

**Acknowledgment.** We thank Professor D. R. Sadoway for the use of his impedance equipment. We thank the Office of Naval Research and the Defense Advanced Research Projects Agency (University Research Initiative) for partial financial support.

**Registry No.** Pt, 7440-06-4; Au, 7440-57-5;  $\text{WO}_3$ , 1314-35-8;  $\text{H}_3\text{PO}_4$ , 7664-38-2;  $\text{H}^+$ , 12408-02-5;  $\text{H}_2\text{SO}_4$ , 7664-93-9;  $\text{NaHSO}_4$ , 7681-38-1;  $\text{H}_2\text{O}$ , 7732-18-5; polyaniline, 25233-30-1; poly(vinyl alcohol), 9002-89-5; aniline, 62-53-3.

(11) Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* 1986, 90, 6080.

## Diffusion of Cesium Ion in $\text{SiO}_2$ Films Derived from Sol-Gel Precursors<sup>1</sup>

Carol L. Schutte<sup>†,‡</sup> and George M. Whitesides<sup>\*,†</sup>

*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Received March 3, 1990

Hydrolyzed tetraethylorthosilicate (TEOS) formed  $\text{SiO}_2$  gel films after being spin-coated onto silicon substrates and heated to temperatures ranging between 200 and 800 °C to effect different degrees of transformation from gel to glass. The index of refraction of the films increased from 1.42 at 25 °C to 1.45 after thermal treatment at 800 °C; the thickness of the films decreased by  $29 \pm 6\%$ . These thermally pretreated gels were coated with a second film of sol-gel-derived  $\text{SiO}_2$  doped with cesium chloride. Diffusion of the cesium ion through the undoped  $\text{SiO}_2$  gels was studied by measurement of the depth profile of cesium by Rutherford backscattering spectroscopy. Increasing the temperature to which the undoped layer had been exposed decreased the extent of its infiltration or diffusion by cesium at room temperature. Diffusion of cesium at high temperature ( $\geq 750$  °C) was, however, independent of the thermal history of the undoped layer, indicating that the rate at which the silica film transforms from gel to glass is faster than that at which cesium diffuses.

### Introduction

The mobility of dopants in  $\text{SiO}_2$  films made from sol-gel precursors—suspensions of silicate particles produced by polymerization involving hydrolysis and condensation reactions of silicon alkoxides<sup>2</sup>—is important in applications

of these films.<sup>3-9</sup> Studies of diffusion in sol-gel systems have focused on diffusion of liquids into porous gels;<sup>10</sup>

(1) Supported in part by the National Science Foundation (CHE-88-12709) and the Defense Advanced Research Projects Agency through the University Research Initiative. The Cambridge Accelerator for Materials Science was purchased and supported (in part) through a DARPA/URI grant and is housed in the Harvard University Materials Science Research Laboratory, an NSF-funded facility (DMR-86-14003).

<sup>†</sup>Harvard University.

<sup>‡</sup>Massachusetts Institute of Technology.

spin-on formulations have provided a phosphorus source for doping silicon through controlled diffusion.<sup>11</sup>

The objective of this work was to study the diffusion of cesium ion—chosen as a representative monovalent cation for its availability and ease of analysis by Rutherford backscattering spectrometry (RBS)—in  $\text{SiO}_2$  films coated on a silicon substrate. The system examined comprised two superimposed layers. The layer adjacent to the silicon substrate originally contained no cesium. It was prepared by coating a sol-gel solution obtained by hydrolysis of tetraethylorthosilicate (TEOS) onto the substrate and heating the resulting film at temperatures between 200 and 800 °C to effect different degrees of transformation from gel to glass.<sup>12</sup> A second film of gel, obtained by addition of cesium chloride to previously hydrolyzed TEOS, was coated onto the first. The two-layer system—one originally free of cesium and the second containing cesium—was heated. The depth profile of the cesium was subsequently determined by RBS. The focus of the investigation was the rate of diffusion of the cesium ion from the doped into the undoped layer and the influence of the thermal history and physical state of the undoped layer on the rate of this diffusion. We wished to define the mildest heating cycle necessary to transform the undoped gel to a coating that acts as a barrier to diffusion of cesium. Previous work has illustrated the usefulness of RBS for studies of high-temperature diffusion in glass and ceramic films: TiC in WC,<sup>13</sup> Fe in  $\text{SiO}_2$ ,<sup>14</sup> and Cu in carbon.<sup>15</sup>

Several factors affect the rate of diffusion of cations in conventional  $\text{SiO}_2$  glasses: the charge of the cation;<sup>16</sup> the amount of water present in the glass;<sup>17</sup> the mobility of the interdiffusing ion or counter anion;<sup>18</sup> the composition<sup>19</sup> and free volume<sup>20</sup> of the glass; the presence and nature of other ions.<sup>21,22</sup>

(2) Klempner W. G.; Mainz, V. V.; Millar, D. M. *Better Ceramics Through Chemistry II*; Materials Science Society, Vol. 73; Brinker, C. J., Clark, D. C., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1986; pp 3–13, 15–25.

(3) Streckert, H. H.; Montgomery, F. C.; Tilley, T. D.; Campion, B. K.; Heyn, R. H. *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; pp 963–972.

(4) Covino, J.; Wilson, C. *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; pp 981–993.

(5) Sim, S. M.; Chu, P.-Y.; Krabill, R. H.; Clark, D. E. *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; pp 995–1010.

(6) Reed, S.; Ashley, C. *Better Ceramics Through Chemistry III*; Materials Research Society Symposium, Vol. 121; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1988; pp 631–634.

(7) Kindred, D. S.; Moore, D. T. *Appl. Opt.* 1988, 27, 492–495.

(8) Moore, D. T. *Appl. Opt.* 1980, 19, 1035–1038.

(9) Yamane, M.; Kawazoe, H.; Yasumorim, A.; Takahashi, T. *J. Non-Cryst. Solids* 1988, 99, 160–167.

(10) Bouaziz, J.; Woignier, T.; Bourret, D.; Sempere, R. *J. Non-Cryst. Solids* 1986, 82, 225–231.

(11) Teh, S. T.; Chuah, D. G. S. *Sol. Energy Mater.* 1989, 19, 237–247.

(12) Klein, L.; Gallo, T. A.; Garvey, G. J. *J. Non-Cryst. Solids* 1984, 63, 23–33.

(13) Rudolf, F.; Jaccard, C.; Chollet, L. *Thin Solid Films* 1980, 65, 331–337.

(14) Wang, P. W.; Feng, Y. P.; Roth, W. L.; Corbett, J. W. *J. Non-Cryst. Solids* 1988, 104, 81–84.

(15) Chang, C. A.; Yee, D. S.; Petkie, R. *Appl. Phys. Lett.* 1989, 54, 2545–2547.

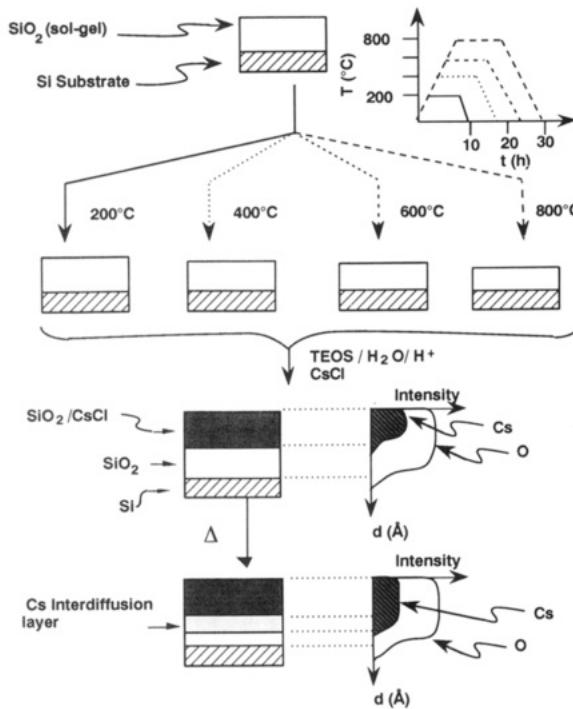
(16) Frischat, G. H. *Glastech. Ber.* 1971, 44, 93–98; Frischat, G. H. *J. Am. Ceram. Soc.* 1969, 53, 625.

(17) Ehrmann, P.; deBilly, M.; Zarzycki, J. *Verres Refrac.* 1964, 18, 164.

(18) Doremus, R. H. *J. Phys. Chem.* 1964, 68, 2212–2218.

(19) Johnson, J. R.; Bristow, R. H.; Blau, H. H. *J. Am. Ceram. Soc.* 1951, 34, 165–172.

(20) Charles, R. J. *J. Am. Ceram. Soc.* 1962, 45, 105–113.



**Figure 1.** Scheme describing the coating and thermal treatment of samples. The  $\text{SiO}_2$  coatings were deposited and heated to either 200, 400, 600, or 800 °C for 2 h each (the temperature–time profiles used are indicated schematically in the upper-right corner), cooled, and coated with the cesium-containing layer. The samples were heated under argon and the diffusion of cesium was monitored by RBS.

Additional factors affect mobility of ions in  $\text{SiO}_2$  made by the sol-gel route, because the structure of the gel changes as it transforms to glass.<sup>12</sup> Between 100 and 110 °C, the gel loses surface water; between 100 and 200 °C, it loses physisorbed water; at approximately 400 °C, residual organic groups are lost by oxidation; up to 700 °C, there is a gradual condensation of Si–OH to Si–O–Si groups with loss of water. One goal of our research was to survey the influence of these changes in the chemical composition and physical structure of the gels on the mobility of cesium ion in them.

The choice of monovalent cesium as a probe ion in our studies was a compromise between the atomic number of the diffusing ion and its mobility (monovalent cations diffuse faster than multivalent cations<sup>16</sup>). We required a heavy ion to be able to measure a signal by RBS without interference from lighter elements in the range of depths  $\leq \sim 8000 \text{ \AA}$ ; we also required an ion that was mobile enough to diffuse at an appreciable rate under accessible experimental conditions.<sup>23</sup>

## Experimental Section

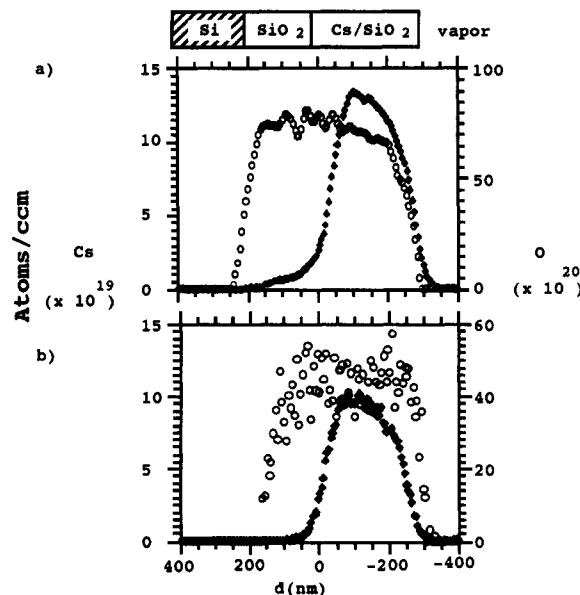
**Materials.** We purchased ethyl ether from Mallinckrodt, hexane from Fisher Scientific, cesium chloride and tetraethylorthosilicate (TEOS) from Alfa, silicon wafers from Monsanto, and absolute ethanol from USI Chemicals Co. All reagents were used without further purification unless noted.

**Preparation of Samples and Conditions for Studying Diffusion.** Figure 1 outlines our experimental protocol schematically. We coated a silicon (100) wafer (2-in. diameter) by pipetting enough (undoped) TEOS solution to cover the wafer (3 mL), spinning the substrate at 1500 rpm for 2 min on a

(21) Lengyel, B.; Boksay, Z. *Z. Phys. Chem.* 1954, 203, 93–112.

(22) Lengyel, B.; Boksay, Z. *Z. Phys. Chem.* 1955, 204, 157–164.

(23) Doremus, R. H. *Glass Science*; Wiley: New York, 1973; pp 167–169.



**Figure 2.** Depth profiles of oxygen (O) and cesium (◆) from unsmoothed data (a, best case; b, worst case). The data in a are for the  $\text{SiO}_2$  undercoat previously heated to  $600\text{ }^\circ\text{C}$  and in b are for the  $\text{SiO}_2$  undercoat previously heated to  $800\text{ }^\circ\text{C}$ . Both samples had no thermal treatment after the cesium chloride doped TEOS was applied.

spin-coater, pipetting more solution onto the coated substrate, and spinning again. The samples were then heated in a programmable furnace at  $1\text{ }^\circ\text{C}/\text{min}$ , held for 2 h at either 200, 400, 600, or  $800\text{ }^\circ\text{C}$ , and cooled at  $1\text{ }^\circ\text{C}/\text{min}$ .<sup>12</sup>

In parallel with these experiments, using the same undoped sol-gel suspension of TEOS, we coated a KBr plate and collected IR spectra at each stage of thermal treatment. The melting point of KBr is  $734\text{ }^\circ\text{C}$ .<sup>24</sup>

Thermogravimetric analysis (TGA) of the unheated coating was carried out on a powder obtained by scraping a film from the silicon substrate with a razor blade.

For studies of diffusion, we recoated the undoped, thermally pretreated  $\text{SiO}_2$  film with a sol-gel suspension prepared by addition of CsCl to previously hydrolyzed TEOS. RBS established the depth profile of cesium. After initial heating of the sample to  $300\text{ }^\circ\text{C}$ , the signal due to chloride in the RBS profile decreased to 40 mol % relative to cesium; by  $700\text{ }^\circ\text{C}$ , it was less than 10%. This observation indicated that chloride ion had volatilized (probably as  $\text{HCl}$ ), and the anionic counterion of the cesium cation had become either  $\text{OH}^-$  or  $\text{O}^{2-}$  (from water) or  $\text{Si}-\text{O}^-$  (from the silicate network).

**Ellipsometry of Samples.** Measurements were made using a thin-film ellipsometer equipped with a He-Ne laser. Thicknesses and indexes of refraction were obtained by using "A FORTRAN Program for Analysis of Ellipsometric Measurement".<sup>25</sup>

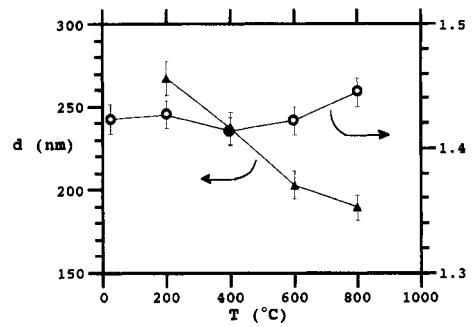
**RBS Analysis.** The depth profiles of cesium were obtained with a 2-MeV  $\text{He}^+$  beam. Depth profiles of cesium and oxygen were calculated by using SPECTRUM ANALYSIS.<sup>26</sup> The depth profiles presented in Figure 7 were smoothed, and representative profiles from unsmoothed data are presented in Figure 2 for comparison.

**Hydrolysis of TEOS.** A solution containing TEOS (61 mL, 273 mmol of Si), ethanol (43 mL), doubly distilled water (5 mL), and aq HCl (0.2 mL of 1 M acid) was heated at  $60\text{ }^\circ\text{C}$  for 1.5 h.<sup>27</sup> After cooling the solution to room temperature, an additional 4.0 mL of doubly distilled water and 12 mL of HCl were added to

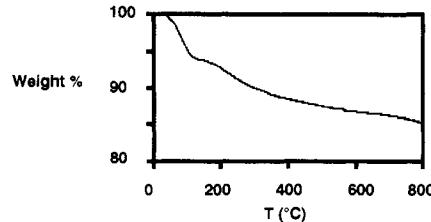
(24) *Handbook of Chemistry and Physics*, 55th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, 1974-1975; p B-121.

(25) "A FORTRAN Program for Analysis of Ellipsometric Measurements" was written by Frank L. McCrackin (NBS). McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Stand. Sect. A* 1963, 67, 363-377.

(26) SPECTRUM ANALYSIS, a FORTRAN program based on algorithms from ref 35, was written by Patrick M. Smith, Division of Applied Sciences, Harvard University.



**Figure 3.** Plot of the index of refraction ( $n$ ,  $\circ$ ) and thickness ( $d$ ,  $\blacktriangle$ ) obtained from ellipsometry of the  $\text{SiO}_2$  films, as a function of the maximum temperature to which they had been heated in air. The temperature profile in the heating is summarized in Figure 1. The lines are included only to guide the eye.



**Figure 4.** Loss of weight from TEOS-derived  $\text{SiO}_2$  as a function of temperature under nitrogen. The temperature of the sample increased at  $10\text{ }^\circ\text{C}/\text{min}$ .

a 100-mL aliquot of the TEOS solution, and the mixture was stored in a freezer ( $-8\text{ }^\circ\text{C}$ ), where it was stable (did not gel) for several months. For coating, the suspension was diluted by a factor of 3 with ethanol (0.62 mmol of Si/mL).<sup>27</sup>

**Preparation of CsCl-Doped TEOS.** To a suspension of previously hydrolyzed TEOS (10 mL, 6.2 mM in Si) was added a water/ethanol (1.8/5.0 v/v) solution of cesium chloride (0.5 mL, 0.265 mM). The solution was coated immediately.

## Results and Discussion

**Characterization of  $\text{SiO}_2$  Films. Ellipsometry of the Supported  $\text{SiO}_2$  Films as a Function of Their Thermal History.** Analysis of the undoped  $\text{SiO}_2$  coatings by ellipsometry, after heating, gave both their thicknesses and indexes of refraction (Figure 3). Data in Figure 3 represent the average values of six measurements; the error bars, 1 standard deviation.

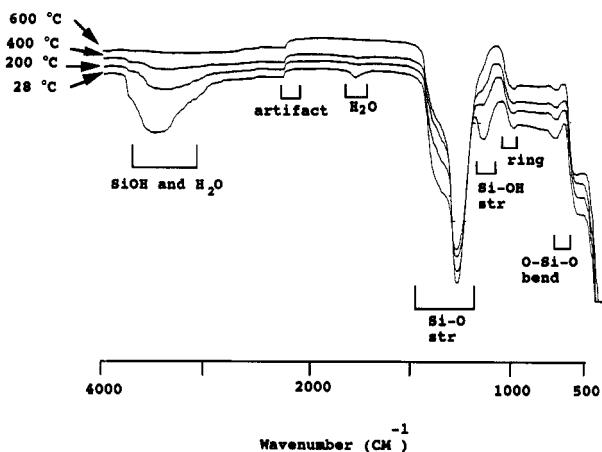
The index of refraction for the  $\text{SiO}_2$  gel prepared at  $25\text{ }^\circ\text{C}$  was  $1.42 \pm 0.01$  ( $98 \pm 1\%$  dense) and  $1.45 \pm 0.01$  ( $99 \pm 1\%$  dense) after heating to  $800\text{ }^\circ\text{C}$  (the index of refraction for dense  $\text{SiO}_2$  glass is 1.46).<sup>28</sup> The room-temperature values of the index of refraction on our spin-coated samples are consistent with measurements on dense dip-coated samples made from a solution of TEOS prepared by the same procedure that we followed.<sup>27</sup> These latter samples had less than 5% porosity,<sup>29</sup> a mean pore volume of less than 4 Å (inaccessible to nitrogen),<sup>30</sup> and a surface area of  $0.93\text{ cm}^2/\text{cm}^2$  of sample.<sup>30</sup> Shear stress increases the density of coatings for formulations designed

(27) Brinker, J.; Keefer, K. D.; Schaefer, D. W.; Assink, R. A.; Kay, B. D.; Ashley, C. S. *J. Non-Cryst. Solids* 1984, 63, 45-59.

(28) Kingery, W. D.; Bowen, H. K.; Uhlmann, D. R. *Introduction to Ceramics*; Wiley: New York, 1976; p 662.

(29) Brinker, C. J.; Hurd, A. J.; Ward, K. J. *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; pp 223-240.

(30) Frye, G. C.; Ricco, A. J.; Martin, S. J.; Brinker, C. J. *Better Ceramics Through Chemistry III*; Materials Research Society Symposium, Vol. 121; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1988; pp 349-354.



**Figure 5.** IR spectra of an  $\text{SiO}_2$  coating on a KBr plate, obtained for samples prepared at room temperature ( $28^\circ\text{C}$ ) and after heating to  $200$ ,  $400$ , and  $600^\circ\text{C}$ .

to give porous coatings,<sup>29</sup> and we expected that shear stress due to spin-coating would contribute to the formation of dense coatings for our samples as well. The index of refraction did not change significantly until the sample was heated to  $800^\circ\text{C}$ .

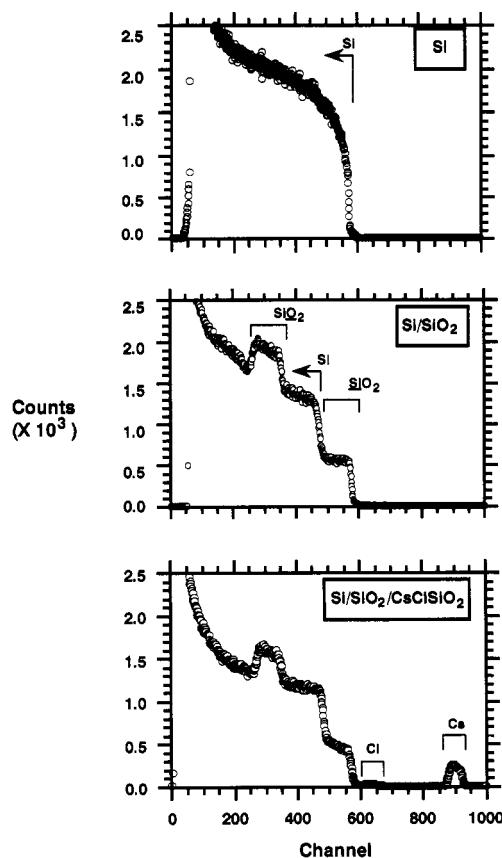
The films decreased in thickness by  $29 \pm 6\%$  on heating to the highest temperature studied ( $800^\circ\text{C}$ ). This decrease in thickness represents a loss of volatiles (water, organics, and possibly low molecular weight silicon containing oligomers). The loss of volatile organosilicon oligomers would allow for the loss of material without a large change in the index of refraction and would be consistent with the unexpectedly small change in the index of refraction over this temperature range.

**Thermogravimetric Analysis (TGA) of the  $\text{SiO}_2$  Coating.** Figure 4 shows the TGA of a gel, heated under nitrogen at  $10^\circ\text{C}/\text{min}$ . The sample had lost  $6.2 \pm 1.5\%$  of its weight by  $200^\circ\text{C}$ , and an additional  $8.5 \pm 1.0\%$  by  $800^\circ\text{C}$ . The rate of loss of weight is faster between  $25$  and  $200^\circ\text{C}$  than between  $200$  and  $800^\circ\text{C}$ . These observations correlate with processes important in the gel-to-glass transition: at  $400^\circ\text{C}$  and below, surface and physisorbed water and organic groups are lost; up to  $700^\circ\text{C}$ , a gradual loss of water results from further condensation of the Si-OH groups.<sup>12</sup> The loss of volatile organosilicon oligomers could occur throughout the thermal treatment until condensation reactions incorporated them into the gel network.

The loss of weight of the sample of  $15 \pm 2\%$ , as measured by TGA, is not consistent with a decrease in film thickness of  $29 \pm 6\%$  with an accompanying decrease in porosity (or increase in density) of  $1.5 \pm 1.0\%$ . These changes in thickness and density would require a loss of weight of  $28 \pm 6\%$ .<sup>31</sup>

**IR Analysis of  $\text{SiO}_2$  Coatings as a Function of Thermal History.** Figure 5 presents IR spectra, collected at room temperature and after each thermal cycle, of an  $\text{SiO}_2$  coating on a KBr plate. Samples were heated at  $1^\circ\text{C}/\text{min}$ , held for  $2\text{ h}$  at  $200$ ,  $400$ , or  $600^\circ\text{C}$ , and cooled at  $1^\circ\text{C}/\text{min}$ .<sup>32</sup> Below  $200^\circ\text{C}$  the decrease in intensity of the

(31) We cannot explain this discrepancy, but speculate that the differences in the conditions under which these samples were heated had a significant effect on these results. In the TGA experiment, the sample form was a powder heated under dry nitrogen at  $10^\circ\text{C}/\text{min}$  from room temperature to  $800^\circ\text{C}$ . In contrast, the samples analyzed by ellipsometry were films heated in ambient air (approximately 70% humidity at  $25^\circ\text{C}$ ) at  $1^\circ\text{C}/\text{min}$ , held for  $2\text{ h}$  at the holding temperature, and cooled at  $1^\circ\text{C}/\text{min}$  to  $30^\circ\text{C}$ .



**Figure 6.** Representative RBS data for (top) the silicon substrate with no coating, (middle) a silicon substrate with an  $\text{SiO}_2$  film, and (bottom) a silicon substrate with an  $\text{SiO}_2$  film under an  $\text{SiO}_2$  film containing cesium chloride.

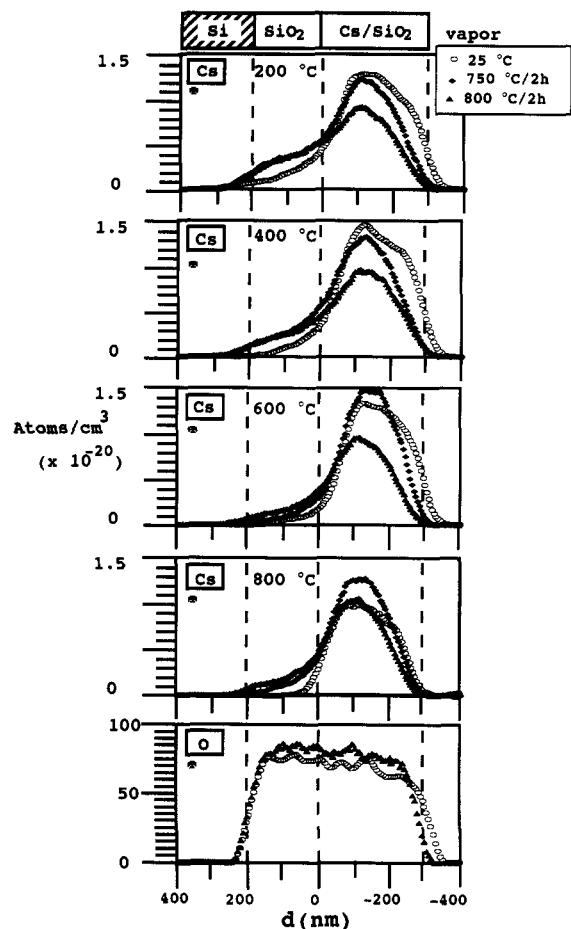
$\text{H}_2\text{O}$  and Si-OH absorbances is consistent with loss of physisorbed water.<sup>33,34</sup> When the sample is heated from  $200$  to  $800^\circ\text{C}$  the decrease in the Si-OH absorbances is consistent with further condensation of Si-OH groups with accompanying loss of  $\text{H}_2\text{O}$ .

**Measurement of the Depth Profile of Cesium in  $\text{SiO}_2$  by RBS.** To examine diffusion of cesium, we heated samples to  $750$ – $800^\circ\text{C}$  under argon. At these temperatures, two processes could, in principle, occur concurrently: transformation (or further transformation, for the undoped  $\text{SiO}_2$  layer) of the silica layer from gel to glass, and diffusion of cesium. By studying the relative rates of migration of cesium into gels that had been carried to different stages of the gel-to-glass transformation by prior heating, we hoped to determine, at least qualitatively, whether diffu-

(32) We attribute the absorbances at  $3600$ – $3400\text{ cm}^{-1}$  to the OH stretching modes of  $\text{H}_2\text{O}$  and SiOH (Maniar, P.; Navrotsky, A.; Rabinovitch, E. M.; Wood, D. L.; Kopylov, N. A. *Better Ceramics Through Chemistry III*; Materials Research Society Symposium, Vol. 121; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1988; pp 323–329); at  $1620\text{ cm}^{-1}$  to the  $\text{H}_2\text{O}$  bend (Maniar, P. *Ibid.*); at  $1180$  and  $1090\text{ cm}^{-1}$  to  $\text{SiO}_2$  network vibrations (Wood, D. L.; Rabinovitch, E. M. *J. Non-Cryst. Solids* 1986, 82, 171–176; Wood, D. L.; Potkay, E.; Clark, H. R.; Kometani, T. *Y. Appl. Spectrosc.* 1988, 42, 299–304); at  $980$ – $950\text{ cm}^{-1}$  to the Si-OH stretch (Walrafen, G. E.; Hokmabadi, M. S.; Holmes, N. C. *J. Chem. Phys.* 1986, 85, 771–776; Walrafen, G. E.; Hokmabadi, M. S.; Holmes, N. C.; Nellis, W. J.; Henning, S. *J. Chem. Phys.* 1985, 82, 2472–2476); at  $800\text{ cm}^{-1}$  to vibrations characteristic of cyclic silica tetrahedra (Tohge, N.; Moore, G. S.; Mackenzie, J. D. *J. Non-Cryst. Solids* 1984, 63, 95–103); at  $550\text{ cm}^{-1}$  to the O-Si-O bend (Tohge, N. *Ibid.*); and at  $440$ – $480\text{ cm}^{-1}$  to O-Si-O bending (Wood, D. L.; Rabinovitch, E. M. *Ibid.* Wood, D. L.; Potkay, E.; Clark, H. R.; Kometani, T. Y. *Ibid.*).

(33) Decottignies, M.; Phalippou, J.; Zarzycki, J. *J. Mater. Sci.* 1978, 13, 2605–2618.

(34) Bertoluzza, A.; Fagnano, C.; Morelli, M. A. *J. Non-Cryst. Solids* 1982, 48, 117–128.



**Figure 7.** Depth profiles for cesium in the two-layer systems summarized in Figure 1. The top four figures show the intensity of the cesium signal as a function of depth. The temperature at which the undoped layer was heated before applying the cesium-doped layer is indicated on each (200, 400, 600, and 800 °C). Each box contains three traces, corresponding to the temperature at which the two-film system was heated to effect cesium diffusion: no heat (20 °C, ○); 750 °C/2 h (◆); 800 °C/2 h (▲). The bottom traces are representative oxygen profiles for samples having both silica films, before and after heating as indicated (○, ▲). This profile defines the aggregate thickness of the silica layer, and demonstrates that cesium does not diffuse into the silicon substrate under our experimental conditions. The size of the errors in individual points are represented on the plots by the error bars.

sion or transformation was faster.

We monitored the diffusion of cesium by RBS. For this system (cesium in  $\text{SiO}_2$ ), the depth resolution of RBS is approximately  $\pm 200 \text{ \AA}$ , and the minimum detectable concentration of cesium is  $0.03 \times 10^{20} \text{ atoms/cm}^3$  (approximately 0.03 atom %, assuming a packing density of  $10^{22} \text{ atoms/cm}^3$ ).<sup>35</sup> Representative plots of RBS data are presented in Figure 6.<sup>36</sup>

Figure 7 shows the cesium profile as a function of the temperature in which the sample had been heated; this figure also shows (bottom) the oxygen profile for unheated and heated samples and provides a direct measure of the total thickness of the two silica films against which the cesium profile can be compared.

(35) Chu, W. K.; Mayer, J. W.; Nicolet, M. A. *Backscattering Spectrometry*; Academic: New York, 1977; p 126.

(36) The chloride signal is small but detectable. We note a progressive decrease in chloride content in the samples with increased thermal treatment. Halide salts could, in principle, be lost from the silica film either as  $\text{HX}$  or, following oxidation from atmospheric oxygen, as  $\text{X}_2$ . An examination of the mechanism of loss of halide ion from sol-gel coatings on heating will be published separately.

To induce detectable diffusion of cesium, the samples were heated under argon by using the same profile as shown in Figure 1: heating and cooling rates of  $1 \text{ }^\circ\text{C}/\text{min}$ , and 2 h at the holding temperature (750 or 800 °C). For calibration, one sample in each set was not heated. We note from the depth profiles of cesium in these samples that the thermal history of the undoped silica layer influences the extent to which cesium infiltrates accessible pores (<5% total porosity) and/or diffuses *before* heating the two-film sample. For example, at a depth of 180 nm (20 nm above the interface between the undoped silica film and the silicon substrate), the cesium content is approximately  $0.1 \times 10^{20} \text{ atoms/cm}^3$  for the sample treated initially at 200 °C for 2 h,  $0.1 \times 10^{20} \text{ atoms/cm}^3$  at 400 °C, and less than  $0.05 \times 10^{20} \text{ atoms/cm}^3$  for samples taken to both 600 and 800 °C.<sup>35</sup>

**Estimation of the Apparent Diffusion Coefficient of Cesium in  $\text{SiO}_2$  Gels.** We estimated the apparent diffusion coefficient,  $D_{\text{Cs}}$  ( $\text{cm}^2/\text{s}$ ),<sup>37</sup> of cesium in the  $\text{SiO}_2$  gel using the thin-film solution.<sup>38</sup> Figure 8 presents the calculated apparent diffusion coefficients. Those for the samples that were previously heated to 200 and 400 °C represent an effective diffusion coefficient, reflecting an aggregate of the room-temperature infiltration of cesium and the diffusion of cesium at elevated temperature. There is no significant difference in the apparent diffusion coefficients calculated for samples previously heated to 200, 400, 600, and 800 °C; they are all in the order of magnitude of  $10^{-15} \text{ cm}^2/\text{s}$ .

(37) For a film with a quantity of solute,  $\alpha$ , diffusing into a material from the surface, the thin-film solution (Crank, *J. The Mathematics of Diffusion*; Clarendon: Oxford, 1975; pp 11-13) is

$$c = \frac{\alpha}{\pi D t} \exp\left(\frac{-x^2}{4 D t}\right)$$

To extract the diffusion coefficient,  $D$ ,  $\ln c$  is plotted versus  $x^2$ . The slope of the line is  $(4 D t)^{-1}$ . The thin-film solution is valid for diffusion into an undoped gel, provided that the gel can be considered infinite; no loss of material occurs through the other side of the film at the  $\text{SiO}_2$  gel/Si interface.

(38) The thin film solution is a reasonable assumption for the estimation of an apparent diffusion coefficient for our system, where a thin film of solute is placed on a "semiinfinite" and solute-free medium. The boundary condition that the flux at the surface is zero ( $dc/dx = 0$  at  $x = 0$ ) satisfies the thin-film solution. The underlying assumptions here are that the diffusion coefficient is not a function of the concentration of cesium and that the driving force to diffusion, the gradient in the chemical potential, is the same as the gradient in concentration—a measurable quantity. The  $\text{SiO}_2$  coating can be considered an infinite medium only if it passes the "leak test." Following Shewmon (Shewmon, P. G. *Diffusion in Solids*; J. Williams Book Co.: Jenks, OK, 1983; p 9): "a short bar can be considered infinite if the quantity of solute which would lie outside its length in a truly infinite bar is an insignificant portion of the total solute present." With 0.1% as the insignificant portion of material to "leak" out, eq 1 is the ratio of the solute that has

$$10^{-3} = \left[ \int_{x'}^{\infty} e^{-x^2/4 D t} dx \right] \left[ \int_0^{\infty} e^{-x^2/4 D t} dx \right]^{-1} \quad (1)$$

diffused beyond the distance  $x'$  to the total content of solute in the bar, where  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $t$  is time (s), and  $x$  is distance (cm). The solution of  $x'$  is  $x' = 4(Dt)^{1/2}$ . For our system, with an apparent diffusion coefficient of  $1.4 \times 10^{-14} \text{ cm}^2/\text{s}$  at an annealing time of 7200 s, there is less than 0.1% diffusion beyond  $\sim 4.2 \times 10^{-6} \text{ cm}$  ( $4200 \text{ \AA}$ ). Our  $\text{SiO}_2$  films extend to approximately  $5000 \text{ \AA}$  from the surface (longer than the minimum length for an "infinite" medium for the given diffusion coefficient and annealing time), and the assumption that the thin-film solution holds is correct. Qualitatively there was little or no diffusion of cesium into silicon (Figure 7).

The  $\text{Si}/\text{SiO}_2$  interface was fixed—no detectable oxidation occurred. Samples were heated in argon to effect diffusion of the cesium at elevated temperatures. There was no significant detectable increase in the depth profiles of oxygen of the films after thermal treatment (see Figure 7, bottom profile).

Since cesium is a charged species, it must either *ion exchange* with another cationic species, for example,  $\text{H}^+$  on  $\text{Si-OH}$ , or diffuse with an anion. Here we cannot examine these processes directly, because we cannot measure  $\text{H}^+$  by RBS.

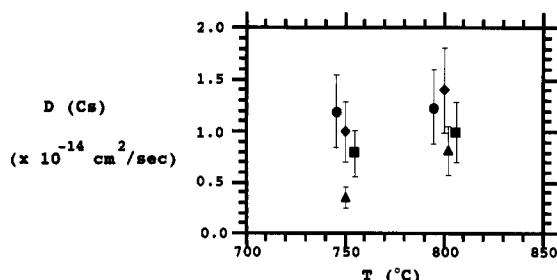


Figure 8. Plot of  $D_{\text{Cs}}$  ( $\times 10^{-14} \text{ cm}^2/\text{sec}$ ) at 750 and 800 °C for samples previously heated to 200 °C (●), 400 °C (◆), 600 °C (■), and 800 °C (▲). The points are shown displaced from the nominal temperatures to avoid overlap.

### Conclusions

Increasing the temperature at which the undoped layer was treated before applying the cesium-containing gel decreased the extent of infiltration into accessible pores and/or diffusion of cesium into the undoped gel at room temperature. This observation indicates that the physical state of the gel (probably its SiOH content) was important in determining ionic mobility. Cesium diffused at room temperature into undoped films that had been heated to 200 and 400 °C but not into those heated to 600 or 800 °C; the extent of diffusion of cesium was greatest for the film heated only to 200 °C. Thus, it seems to be necessary to have heated the undoped film to approximately 600 °C to prevent infiltration and/or diffusion of cesium into it when it is overcoated with a cesium chloride containing gel layer at room temperature.

The rate of diffusion of cesium in the undoped gel correlates qualitatively with the concentration of SiOH groups in this gel, as measured by IR spectroscopy.<sup>39</sup> At

(39) The SiOH content in a glass can strongly influence its properties. Incorporation of 0.1 wt % water in  $\text{SiO}_2$  reduces its viscosity by 3 orders of magnitude at 1000 °C. The Si-OH groups may bind  $\text{Cs}^+$  (plausibly as  $\text{SiO}^-\text{Cs}^+$ ) and increase its mobility. Doremus, R. H. *Glass Science*; Wiley: New York, 1973; pp 170–172.

room temperature, the gels retained chloride ion, and part of the relatively high room-temperature mobility of cesium ion into the undoped gels that had not been heated to temperatures greater than 400 °C may be due to the presence of both cation (cesium) and anion (chloride) in this system in diffusible form. Since the chloride ion rapidly disappears (to 37% of the concentration of cesium by 300 °C and approximately to 10% by 700 °C) from the gel, we assume the counterion for most of the cesium ion at high temperature is either  $\text{SiO}^-$  or  $\text{O}^{2-}$  at temperatures above 300 °C.

Cesium diffusion was negligible at  $T < 750$  °C. When detectable migration of cesium did begin to occur ( $T \geq 750$  °C), its rate was independent of the thermal history of the undoped layer over the range of temperatures used in treating these layers (200–800 °C). The extent of diffusion of cesium at elevated temperatures did not depend on the temperature of thermal pretreatment of the undoped gel. Thus, when the sample reached a temperature at which detectable diffusion of cesium occurred ( $T > 750$  °C), the cesium "saw" silica film previously heated to any temperature between 200 and 800 °C as having the same physical state. We infer from this observation that the rate at which the silica film transforms from gel to glass is fast relative to cesium migration, at the high temperatures required for this migration to be detectable by RBS.

**Acknowledgment.** Professor Roy Gordon and Jianhua Hu assisted in ellipsometric analyses. We thank Professor Andy R. Barron and A. Applett for the TGA analysis. C.L.S. acknowledges financial support from the American Association of University Women through a Dissertation Fellowship (1988–1989). We are grateful to Professor Greg Ferguson (Lehigh University) for valuable discussions. John Chervinski was very helpful in assisting with the RBS measurements.

**Registry No.**  $\text{Cs}^+$ , 18459-37-5; vitreous silica, 60676-86-0.