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Influence of the wettability of silicon substrates on the thickness of sol–gel silica films

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The fabrication of thick optical films by spinning from solution on silicon substrates is an important technique for integrated optics applications. In particular, several authors have studied the conditions under which the thickness of sol–gel silica films deposited on silicon wafers from solutions of water, tetraethoxysilane (TEOS) and ethanol can be maximized. The influence of processing parameters, such as composition, ageing period of the solution and spinning rate, have been studied. The effect of the wettability of the silicon substrate on the film thickness was investigated. The wetting characteristics of the silicon surface may be changed by adequate chemical cleaning methods. The hydrophilic wafers obtained by controlled oxidation of the silicon were found to have greater affinity to the film forming solution and to lead to thicker films than hydrophobic wafers obtained by etching the silicon surface with HF solution.

1. Introduction

Silicon wafers are commonly used as substrates in many applications, mainly in the electronics industry. The widespread use of silicon single crystals as substrates for optical films, e.g. sol–gel silica films [1–4], is justified by their flatness and transparency in the infrared region. However, the structure of the SiO_2/Si interface is difficult to characterize due to the chemical nature of the silicon surface. Polished silicon undergoes spontaneous oxidation and it becomes easily contaminated during processing or exposure to the environment.

Many researchers [5–8] have developed cleaning methods which depend on their specific purposes. For example, the RCA-type cleaning consists of oxidation of the organic contaminants with a solution of $H_2O:H_2SO_4$ followed by etching with hydrofluoric acid. The resulting surface may still have physical and chemical heterogeneities which can be minimized by repeating the oxidation and etching procedures. The changes in the state of the silicon due to the cleaning process may be assessed by wetting and XPS studies.

The aim of the present work was to study the influence of the wetting characteristics of the silicon substrates on the thickness of sol–gel silica films. These films, which are used in integrated optical devices, may be obtained by spinning drops of a solution of tetraethoxysilane (TEOS), ethanol and water on silicon substrates. Matos *et al.* [2] studied possible conditions to maximize the film thickness. Taking their conclusions into account, we paid special attention, in the present work, to the interface between the film-forming solution and the silicon.

First, we studied the relationship between the wettability and the chemical composition of the silicon surface. Second, we related the wetting behaviour of the solutions to their composition. Finally, we tried to correlate the thickness of the films obtained by the spinning technique with the wettability of the silicon substrates.

2. Experimental procedure

The silicon wafers used were n-type, ⟨1 1 1⟩ orientation, from Virginia Semiconductors.

The cleaning procedure, which may be described by the following sequence of steps, was a simplification of the standard RCA clean [5]:

1. immersion of the sample in a solution of $H_2O_2(1):H_2SO_4(1)$ for 10 min;
2. dip in a solution of $HF(1):H_2O(9)$ for 30 s;
3. immersion in H_2SO_4 for 10 min;
4. dip in the above solution of HF for 30 s.

All steps were separated by rinses with deionized water and, after the final rinse, the wafers were dried with nitrogen.

The chemical composition of the silicon wafers at different stages of the cleaning procedure was determined by X-ray photoelectron spectroscopic (XPS) analysis in the Centro de Química-Física Molecular of Universidade Técnica de Lisboa. The samples were analysed with a magnesium X-ray source in a Kratos DS800 photoelectron spectrometer.

The wetting studies were carried out using a Ramé–Hart goniometer at room temperature. The substrates were kept inside an ambient chamber saturated with the liquid sample.

The sol–gel films were obtained from solutions of TEOS (Alfa Products, 99%), deionized water and ethanol (Merck absolute, p.a.). Several solutions were

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prepared with different water/TEOS molar ratios, R. A small amount of HCl was added to adjust the pH to 2.5 or 0. The solutions were heated and continuously stirred up to $\approx 70\,^{\circ}C$. Ageing of the solutions was achieved by letting them stand for several days.

The films were obtained using a Headway Research, Inc. photo resist spinner to rotate a few drops of solution deposited on the silicon wafers with a spinning rate of 2500 r.p.m. during 30 s. The coated wafers were kept in covered petri dishes inside a desiccator. The thicknesses of the resultant films were measured with a Sloan Dektak IIA profilometer.

3. Results

3.1. Correlation between wettability and chemical composition of the silicon surface

The silicon wafers were obtained from silicon single crystals which were sliced with a saw blade following the procedure given by Coldaser [9]. After the sawing process, the roughness of the surface was eliminated by polishing with an etchant solution. Finally, the wafers were cleaned to remove the residues of the polishing compound. The reproducibility of the silicon surfaces obtained by this method is not perfect.

The contact angle of deionized water drops was measured on seven new wafers and the values varied between 35° and 43°. These values are averages of ten measurements performed on three drops deposited on each wafer.

The wettability of the wafers changed during the cleaning procedure. The contact angle of deionized water was measured at the end of each step of the cleaning sequence and the results are shown in Table I.

The values of the contact angles show that, when silicon was oxidized (steps 1 and 3), the surface became more hydrophilic due to the presence of silanol groups. In contrast, etching with hydrofluoric acid (steps 2 and 4) generated Si–F bonds which increased the surface hydrophobicity [10].

The chemical composition of the silicon surface before cleaning and at the end of steps 1 and 2 was analysed by XPS. Elemental compositions of O (1s peak), Si (2p peak) and F (1s), obtained with an angle of incidence of 45°, are shown in Table II. As expected, the percentage of oxygen atoms was maximum for the oxidized surface (step 1) and minimum for the etched surface (step 2). Initially, the surface of the wafer contained a very small amount of fluorine atoms, resulting from the method of industrial preparation of the wafers. The number of fluorine atoms decreased after oxidation and increased again by etching with hydrofluoric acid.

It was found previously [2] that the best silicon substrates for the sol–gel films were obtained simply by etching with a 12% solution for HF (by volume) and rinsing with deionized water. The contamination of etched silicon surfaces in air at room temperature was studied by Archer [11] and Raider *et al.* [10]. In order to determine the surface activity of the present wafers, we measured the contact angles of water drops deposited on silicon substrates at several times after the cleaning procedure. Fig. 1 shows these contact angles as a function of the logarithm of the time of exposure to ambient of five etched samples. During the first 17 h, the contact angles did not vary significantly with time but, at the end of 168 h, an average decrease of 8° was observed. These results are consistent with the conclusions of Raider *et al.* [10]. They reported that etching the silicon surface enhanced the adsorption of organic impurities which prevented the oxidation. The oxide growth which should be responsible for the decrease in the contact angle of water, began after a period of induction.

TABLE I Average contact angles of water drops on wafers during the cleaning process

Step	Average contact angle (deg)
1	20 ± 1
2	69 ± 6
3	32 ± 5
4	68 ± 6

TABLE II Elemental compositions found by XPS

	O (1s)	Si (2p)	F (1s)
Initial	52.9	46.6	0.44
Step 1	56.6	43.1	0.36
Step 2	22.4	76.2	1.40

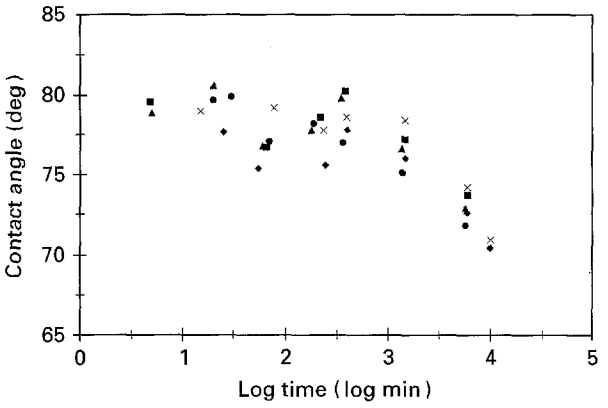

Figure 1 Average contact angle of water on etched silicon wafers as a function of the logarithm of the time of exposure to the ambient.

3.2. Correlation between wetting behaviour and composition of film-forming solutions

The influence of the composition of the film-forming solutions (ethanol + TEOS + water) on their wetting behaviour was studied by measuring the contact angles of drops of different solutions deposited on etched silicon substrates.

Fig. 2 shows the average contact angle obtained on three wafers as a function of R = (number of moles of water)/(number of moles of TEOS). Although the error bars are large due to the uncertainty in the

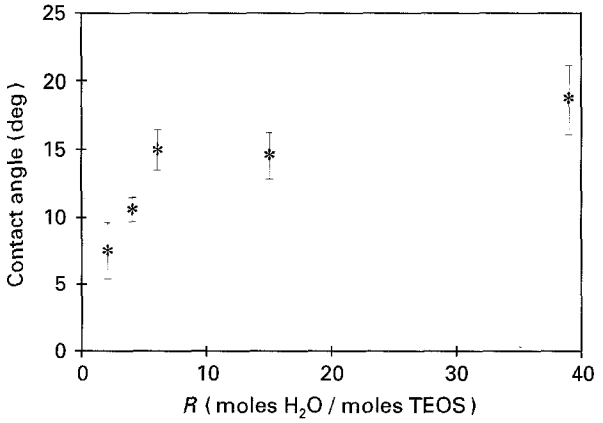

Figure 2 Average contact angle of film-forming solutions on etched silicon as a function of R (number of moles of water/number of moles of TEOS).

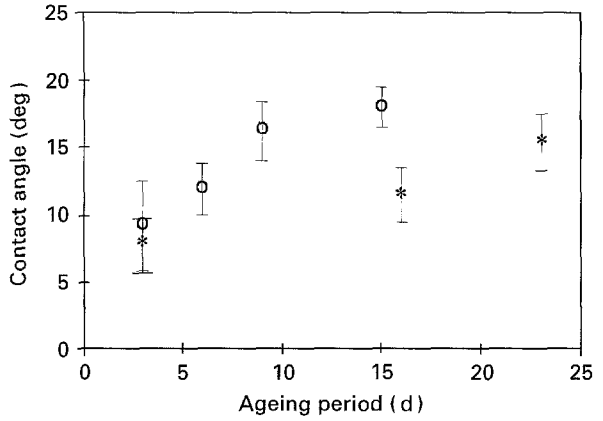

Figure 3 Average contact angle of two film-forming solutions on etched silicon as a function of their ageing time: (○) $R = 2$ pH = 0; (*) $R = 2$ pH = 2.5.

measurement of these small contact angles, there is a definite trend for an increase in the contact angle, θ, as R increases, i.e. as the amount of water increases.

The effect of the ageing period of the solutions on the contact angle was studied for two solutions with the same $R = 2$, but different values of pH (0 and 2.5). The contact angles are plotted as a function of the ageing time in Fig. 3. For both solutions, the wettability decreases as the ageing time increases.

The results in Fig. 3 also show that a pH variation from 2.5 to 0 produces a decrease in the wetting properties of the solution.

3.3. Correlation between film thickness and wettability of the substrates

The main aim of this work was to determine the effect of the wettability of silicon wafers (which is rather dependent on the history of the surface), upon the thickness of sol–gel silica films.

To study this effect, we deposited films from a solution with $R = 2$, 59% volume in TEOS and pH = 2.5, aged for a period of 7 days, on wafers with different wettabilities. Two types of wafer were prepared: using the oxidation step ($H_2O_2 + H_2SO_4$ solution) and the etching step (HF solution) of the RCA clean. According to the results shown in Table I, the oxidized wafers are more hydrophilic than the etched wafers.

TABLE III Influence of surface treatment on film thickness

Thickness, h (μm)	
Hydrophilic	Hydrophobic
1.028	0.943
1.119	0.978
1.054	0.938
1.204	1.070

Table III shows the measured film thickness on two sets of four wafers: one set was hydrophilic and the other set was hydrophobic, depending on the surface treatment. The uncertainty associated to these values is not larger than 8%. In spite of the scatter of the experimental values, this result suggests that hydrophilic wafers produce thicker films, 12% higher on average, than hydrophobic ones.

4. Discussion

The thickness of films produced by centrifugal spinning on rotating discs depends on a variety of factors. According to the model of Meyerhofer [12], the film thickness, h, shows the following dependence on spin speed, f, initial viscosity, v_0 and evaporation rate e:

$$h \propto f^{2/3} v_0^{1/3} e^{1/3}. \quad (1)$$

The rate of change of the volume of the solution deposited on the substrate depends on outflow and evaporation. At the start, the outflow dominates, but, when the film thickness drops to about one-third of the initial value, flow ceases due to the high viscosity and only evaporation continues. Moreover, the film thickness should also depend on the wettability of the solid surface. Ingram [13] studied the wetting of silica by n-alkanes and found that the liquids which completely wet the silica form the thickest films.

In qualitative terms, we can interpret the increase of film thickness produced on highly wettable substrates as the result of the decrease of the liquid outflow due to a strong solid/liquid interaction.

The variation of the contact angle with the pH of the solution suggests that the wettability depends on the ionization of the surface functional groups. The surface of etched silicon wafers after being rinsed with water and exposed to ambient air, present Si–OH groups which interact with the water phase of liquid drop [14]. At low pH values, the Si–OH groups present on the silicon surface are assumed to be undissociated and the interaction with the aqueous solution is small, whereas at higher pH the functional groups begin to dissociate and the contact angle decreases.

The increase of the contact angle with the ageing time of the solution can be related to the chemical modifications occurring in the bulk liquid [15]. However, this relationship is not easy to establish, due to the complexity of the process. Initially, the molecules of TEOS are hydrolysed and water is consumed; after a period of time, which can be short or long depending on the value of R, two possible condensation reactions start, producing either water or ethanol. However, the

observed increase in viscosity with time [2] suggests a simultaneous increase in the surface tension of the solution, which may be responsible for the increase in the contact angle.

The increase of the contact angle with R (the water/TEOS molar ratio in the solution) can be related to the fact that water is the only component which meets the silicon surface with a finite contact angle.

In conclusion, we studied the dependence of the wettability of the silicon substrates on the cleaning procedure and the relationship between the composition of the film-forming solution and its wetting behaviour. We found that the minimum contact angle was obtained for the solution with the smallest value of R ($R = 2$) and the highest pH (pH = 2.5) deposited on an oxidized (hydrophilic) wafer. Finally, the relationship between the wetting characteristics of the film-forming solution and the thickness of the resulting film was established: spin-coating deposition on hydrophilic silicon wafers of maximum wettability leads to the thickest films.

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