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An etch rate study on thermally annealed SiO_2 films deposited in a TEOS–LPCVD system

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The etch rate behaviour of tetraethylorthosilicate (TEOS)–SiO_2 films was investigated as a function of annealing parameters (time, temperature and ambient pressure). The etch rate of TEOS–SiO_2 films depends strongly on annealing pressure within the temperature range 750 to 900° C, while the etch-rate behaviour of films thermally annealed at 1000° C is mainly controlled by the thermally activated rearrangements of SiO_4 tetrahedra from as-deposited films in a closed structure to that of thermally grown SiO_2 films. The etch-rate behaviour of thermally annealed TEOS–SiO_2 films is interpreted in terms of the chemical change of the film structure.

1. Introduction

The etch-rate behaviour of the chemically vapour deposited SiO_2 films is important for practical applications as well as a better understanding of the nature of these films [1, 2]. The purpose of this work was to study the etch-rate behaviour of tetraethylorthosilicate (TEOS)–low pressure chemical vapour deposition (LPCVD)–SiO_2 films with annealing parameters (temperature, time and pressure) and to interpret these results in terms of structural modifications of the SiO_2 network [3–6].

2. Experimental procedure

The silicon substrates, 2 in. (~ 5 cm) diameter, were cleaned in H_2SO_4/HNO_3 solution in deionized water, at 80° C and then dipped in 5% HF solution.

The SiO_2 films were deposited by the decomposition of TEOS in a LPCVD reactor at a temperature of 750° C and a pressure of 0.4 torr [7]. After annealing the SiO_2 films in vacuum or dry N_2 within the temperature range 750 to 1000° C, the film thicknesses were measured using an ellipsometer.

The etch rate in p-etch solution (2 parts 70% HNO_3 + 3 parts 49% HF + 60 parts H_2O by volume) was determined as shown previously [8], at an etching temperature of 20° C.

3. Results

The etch rate curves of thermally treated SiO_2 films plotted against densification time at 750° C show a higher etch rate for the films annealed in vacuum compared to those annealed in dry N_2, the difference between the two curves increasing with densification time, and in both cases the etch rate decreases when the densification time increases (Fig. 1, curves 1 and 2). On the other hand, for densification times above 10 min, the SiO_2 films annealed at 1000° C show a slightly higher etch rate for films treated in vacuum, compared to those treated in dry N_2, and for densification times greater than 30 min the etch rate tends towards that of the thermal oxide: 0.2 nm sec^{-1} [4] (obtained in p-etch solution at a temperature of 25° C; Fig. 1, curves 3 and 4).

In addition, the SiO_2 films annealed for 30 min in vacuum show a higher etch rate compared to the films annealed for 30 min in dry N_2 when the densification temperature is varied in the 750 to 1000° C range (Fig. 2, curves 1 and 2). It should be mentioned that the etch rate of SiO_2 films annealed in vacuum shows a continuous decrease when the temperature increases from 750 to 1000° C, while for films annealed in dry N_2 the etch rate decreases for temperatures in the 750 to 800° C range and at temperatures in the 800 to 1000° C range the etch rate attains a constant value of 0.2 nm sec^{-1} (Fig. 2, curves 1 and 2).

4. Discussion

The etch rate behaviour of the thermally annealed SiO_2 films deposited in a TEOS–LPCVD system will be interpreted in terms of the structural change of the films with the annealing parameters (time, temperature and pressure).

It should be mentioned that the silicon dioxide film obtained by chemical vapour deposition or sputtering techniques, has an amorphous structure consisting of SiO_4 tetrahedra similar to that of fused silica or thermally grown silicon dioxide film, but the arrangements of SiO_4 tetrahedra in as-deposited film is more irregular than that in the heat-treated film or thermally grown silicon dioxide film [3]. On the other hand, a large etch rate of a deposited film results from an unstable structure, the dangling bonds of the silicon or oxygen atoms in the film structure increasing the reactivity of the SiO_2 network with the etch solution during the etching process, while the decrease in etch rate on annealing may be explained by a narrowing of the width of the angle distribution of the Si–O–Si bonds or by bonding of isolated SiO_4

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tetrahedra [3], and by inducing the reduction reaction of radicals incorporated into the film during deposition of SiO_2 [2].

On the other hand, the water formed during the decomposition of TEOS ($SiO_4C_8H_{20} \rightarrow SiO_2 + 4C_2H_4 + 2H_2O$) in a chemical vapour deposition reactor is incorporated in the structure of as-deposited SiO_2 films as Si–OH groups or physically adsorbed water as revealed by infrared adsorption bands at a wavelength of 3650 and $3400\,cm^{-1}$, respectively [4]. However, the adsorption band at 3400 to $3600\,cm^{-1}$ of as-deposited SiO_2 film was reduced by a temperature anneal at high temperature around 1000° C to a very weak adsorption band at $3660\,cm^{-1}$ similar in intensity and position to that observed in undried steam-grown oxides [4].

Therefore, during the annealing process of TEOS–SiO_2 films, the removal of SiOH and HOH groups from the film structure takes place [4, 6]; this favours a rearrangement of the SiO_4 tetrahedra to a more stable structure from a chemical point of view, which determines a low etching rate of the annealed film in comparison with that of as-deposited film.

From the above statements and by analysis of Figs 1 and 2 it may be concluded that, in general, the lower etch rates obtained for TEOS–SiO_2 films thermally annealed in dry N_2 at atmospheric pressure in comparison with vacuum-annealed films, indicates that the bonding of the SiO_4 tetrahedra in a more stable structure of an SiO_2 network (without dangling bonds of silicon or oxygen atoms and radicals) will take place in a more efficient way by increasing the annealing temperature and/or annealing pressure.

Thus, annealing for 1 h at 1000° C in dry N_2 or vacuum (Fig. 1, curves 3 and 4) is sufficient to rearrange the SiO_4 tetrahedra in a stable structure close to that of thermally grown SiO_2, this fact being evinced by an etch rate in the region of $0.2\,nm\,sec^{-1}$, the etch rate obtained for thermally grown SiO_2 [4]. On the other hand, the decreasing thickness of TEOS–SiO_2 film annealed for 1 h in dry N_2 at temperatures in the 750 to 1000° C range was found to be below 4% [2], a similar behaviour being observed for SiO_2 films deposited in the SiH_4–O_2–N_2 system at atmospheric pressure and low temperature (T = 400° C) for which a thickness reduction of about 10% was obtained for an annealing time of 1 h in dry N_2 at 1000° C [6], this behaviour seems to exclude a significant density change of thermally annealed TEOS–SiO_2 films [2] while the etch rate shows a strong decrease by about five times for thermally annealed SiO_2 films at 1000° C in comparison with as-deposited films (Fig. 1, curves 3 and 4). Therefore, the annealing of the TEOS–SiO_2 films for 1 h in dry N_2 or vacuum at 1000° C results mainly in a modification of the film chemistry [2] (rather than a physical change) via a thermally activated reaction between isolated SiO_4 tetrahedra [3], which leads to the bonding of the randomly distributed tetrahedra in a structure close to that of the thermal oxide, the rearrangement process of SiO_4 tetrahedra from as-deposited film being favoured by the viscous flow phenomenon which appears in the SiO_2 film at temperatures above 950° C. In fact, the

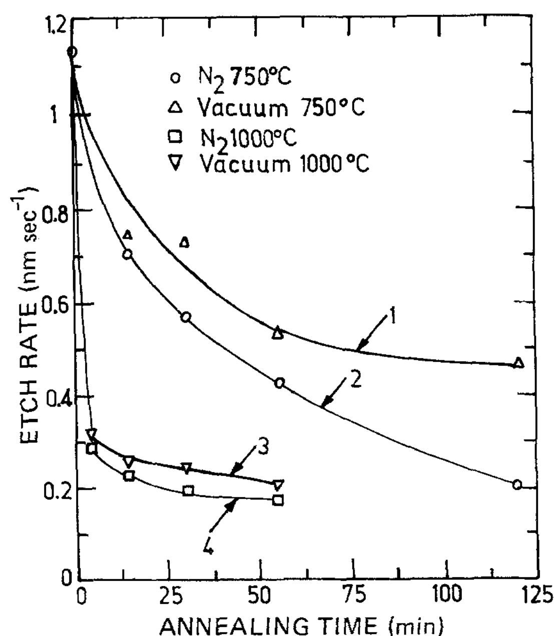

Figure 1 The variation of etch rate of TEOS–SiO_2 films with densification time, annealing temperature (T) and pressure: (1) T = 750° C in vacuum; (2) T = 750° C in dry N_2; (3) T = 1000° C in vacuum, (4) T = 1000° C in dry N_2.

etch rates of SiO_2 films thermally annealed for 1 h at 1000° C in dry N_2 and in vacuum have similar values, close to the value of $0.2\,nm\,sec^{-1}$ of the etch rate of thermal oxide [4].

For SiO_2 films heat treated at 1000° C in dry N_2 or vacuum the etch rate shows a rapid decrease with annealing time in the first 10 min of the annealing process (Fig. 1, curves 3 and 4). Thus, it should be concluded that a significant percentage of the rearrangement of SiO_4 tetrahedra from as-deposited SiO_2 film takes place rapidly in the first 10 min of the annealing process. On the other hand, for annealing times above 10 min, the SiO_2 films annealed at 1000° C in vacuum exhibit a slightly higher etch rate than the films annealed in dry N_2, the values of the etch rate in both cases tending slowly towards the etch rate of the thermal oxide of $0.2\,nm\,sec^{-1}$ (Fig. 1, curves 3 and 4).

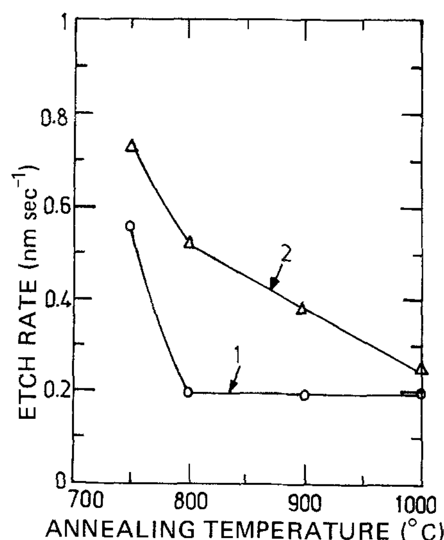

Figure 2 The variation of etch rate of TEOS–SiO_2 films with densification temperature, annealing pressure and time: (1) in dry N_2 for 30 min, and (2) in vacuum for 30 min.

The variation of etch rate with annealing temperature obtained for a constant annealing time of 30 min shows a strong dependence on annealing pressure. Thus, the etch rate of the SiO_2 films annealed in vacuum shows (Fig. 2, curve 2) a continuous decrease with temperature in the 750 to 1000° C range, while for films annealed in dry N_2, the etch rate (Fig. 2, curve 1) decreases only for a temperature increase in the 750 to 800° C range, and then levels off (in the 800 to 1000° C range) at a value of 0.2 nm sec^{-1} close to that of thermally grown SiO_2 film, the difference between the etch rate values of curves 2 and 1 (Fig. 2) showing an increase–maximum–decrease variation with annealing temperature (with a maximum at 800° C). Thus, from the above statements it may be concluded that the annealing pressure plays an important role in the process of rearrangements of SiO_4 tetrahedra from as-deposited SiO_2 films for annealing temperatures in the 750 to 900° C range. Therefore, the annealing pressure may be an important parameter in the annealing process of silica glasses in addition to the annealing temperature and annealing time.

5. Conclusions

The etch-rate variation of TEOS–SiO_2 films in the temperature range 750 to 900° C is strongly influenced by the annealing pressure which is an important parameter in addition to the annealing temperature and time, while at a temperature of 1000° C the etch-rate behaviour is mainly controlled by a thermally activated rearrangement of SiO_4 tetrahedra from as-deposited SiO_2 film in a closed network, to that of thermally grown SiO_2, this process being essentially independent of the annealing pressure.

The large etch rate of the deposited film results from the unstable structure of the SiO_2 film which contains chemically active species such as dangling bonds of silicon or oxygen atoms, SiOH and HOH impurities and an arrangement of SiO_4 tetrahedra in an irregular structure, while the low etch rate of thermally annealed SiO_2 films results through the removal of chemical impurities as SiOH or HOH from the film structure and the rearrangement of SiO_4 tetrahedra into a more stable structure.

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