Near surface modification of silica structure induced by chemical/mechanical polishing

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Planarization of dielectric materials in multilevel devices has become an important topic in recent years. Planarization achieved through chemical/mechanical polishing (CMP) is the foremost of the techniques available to provide an appropriate low-topography surface for accurate lithography. In this study the effects of the planarization process on deposited SiO_2 films, a material to which CMP is frequently applied, have been examined. The analysis, completed using transmission electron microscopy and Fourier-transform infrared spectroscopy, revealed evidence of chemical/structural modification of the SiO_2 to 100–200 nm from the polished surface and more heavily altered or deformed regions extending to a few tens of nm in depth.

1. Introduction

As the drive in advanced microprocessor development is directed toward smaller features and multiple device levels, new technologies are developed to address the demands of new designs. In order to successfully manufacture a proposed multilevel metallization design, planarization is required for accurate lithography. In recent years this demand has prompted the development of chemical/mechanical polishing (CMP) as a planarization technique. However, the technique has outdistanced the science with polishing "recipes" developed empirically for each specific process with little understanding of the mechanisms at work or the impact on the remaining material.

This importance of understanding the effects of CMP is significant, considering that the extent of water penetration into the silica is of the order of the thickness at which the films are used (100–1000 nm). Concerns about detrimental effects include low breakdown voltage, device contamination and delamination of subsequent metallization. The objective of this study was to investigate material having undergone CMP processing and identify any detectable effects on the film structure and chemistry.

A regular application of CMP in device fabrication is for planarization of the interlevel dielectric, usually SiO_2, using an aqueous, submicrometre fumed silica dispersion. It is appropriate to first consider the interaction of this slurry chemistry in general before applying it to the CMP process. Contrary to what might be expected, silica is very reactive with water, at least at the interface of contact. Where the three-dimensional network of $[SiO_4]^{4-}$ units comes into contact with molecular water a hydration reaction occurs between H_2O and the siloxane (Si–O–Si) bond. In the general mechanism [1], schematically outlined in Fig. 1, a water molecule orients in response to the polarized $Si^{(+)}$–$O^{(-)}$ bond (Fig. 1a) and the original Si–O and

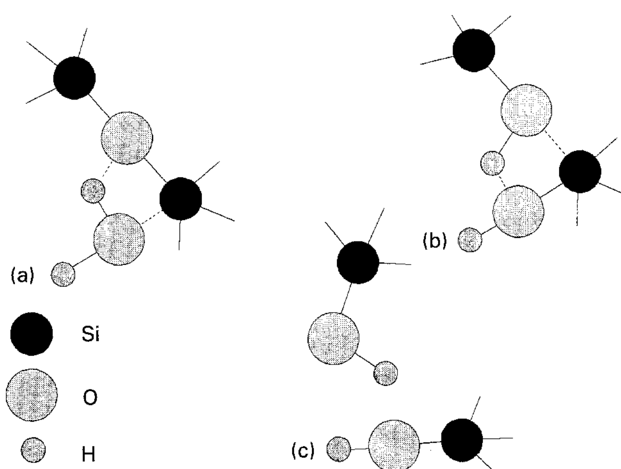

Figure 1 A schematic of the hydration mechanism of the siloxane bridge.

H–O–H bonds transfer (Fig. 1b), resulting in two hydroxylated silicon molecules (Fig. 1c). Note that dissolution of silica occurs if all four bridging oxygen bonds are hydrated, producing the solute species $Si(OH)_4$ (silanol).

The above reaction is one of the active mechanisms in silica polishing. For the case of a non-reactive polishing particle moving over a silica surface, dissolution takes place at the leading edge of the particle due to an increased liquid temperature, higher solubility due to curvature (analogous to the Gibbs–Thompson effect) and compressive stress in the glass network. The opposite reaction occurs on the trailing edge of the particle for converse reasons (lower temperature, curvature reduced solubility and tensile stress) causing precipitation, ultimately producing little net change [2]. Therefore, unless there is a mechanism to remove the dissolved species or alter the

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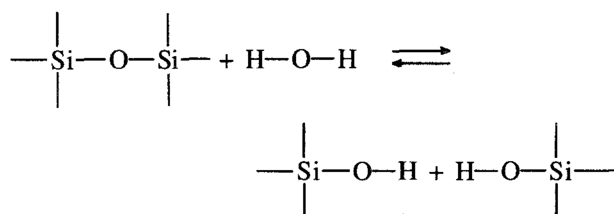
balance of the following reaction,



in favour of the forward direction, the material removal rate will be negligible.

For a reactive slurry particle, such as CeO_2, a mechanism exists in which a non-bridging oxygen in the silica ($Si–O^{(-)}$) reacts with a hydroxylated cation (M) (see [2] for a more detailed description). If the O–M bond is stronger than the opposing Si–O bond (or any single Si–O bond linking the associated tetrahedral unit to the bulk network) the Si–O bond will rupture, effecting material removal from the surface.

In the microelectronics industry, CMP of the SiO_2 interlevel dielectric is performed using fumed silica particles as an abrasive. Although not entirely non-reactive, silica is not effective in material removal by the reactive species since the opposing bonds in the glass and particle are both Si–O bonds, making net removal by particle contact negligible. As mentioned previously, extensive hydration resulting in dissolution can occur at the silica/water interface. This does not normally occur to a great extent because the solubility of the reaction product, silanol, is low in water with a neutral pH, quickly slowing the reaction. However, at a pH of more than $\sim$ 10.0 the solubility of silanol in water increases sharply [3], allowing dissolution ahead of the particle without redeposition at the trailing edge, thus favouring the dissolution reaction in the forward direction resulting in material removal.

The strain on the network has an influence on the reaction of water with the siloxane bond by reducing the energy necessary to break the Si—O bond in the mechanism described in Fig. 1, thus increasing the reaction rate [4]. The contact of the abrasive silica particles with the film surface transmits strain some distance into the bulk network which could translate to a gradient in the degree of reaction and ultimately to a gradient in the structure of the near-surface oxide. A grazing angle X-ray study of polished silica provided evidence to support such a relationship [5]. The study determined the existence of a 2 nm surface region possessing lower density than the bulk, below which the density increased to a value greater than the bulk, gradually returning to the bulk density at a depth of 15–20 nm below the surface. The authors postulated that the thin surface region was a highly hydrated, loosely bound network, while the deeper region was a plastically compressed network resulting from the stress of contact with the abrasive particles.

2. Experimental and analysis

The polishing experiments were conducted with 5 inch silicon wafers with as-deposited PECVD oxide films and on films having undergone a 60 s, 1000 °C rapid thermal anneal using a Strasbaugh 6CU polisher. The polishing slurry consisted of a submicrometre fumed silica dispersion in water with KOH added to give a pH of 10.3–10.5. The temperature of the polishing platen was 30–35 °C.

The films were analysed using transmission electron microscopy (TEM) and Fourier-transform infrared (FTIR) spectroscopy to characterize structural and chemical variation. FTIR spectroscopy is highly sensitive to structural variation, providing accurate information on the range of bonding structures in the interaction volume of the sample, however, it cannot localize this information to a specific part of the film. TEM analysis can identify spatial variations in structure but cannot easily determine the specific nature of the structure, making these two techniques complementary in the type of information they provide.

Silica films having undergone the CMP process were sectioned and prepared for cross-sectional TEM analysis. The TEM micrographs, shown in Fig. 2, exhibited surface variations observed on two scales. Repeated sample preparation indicated that the specimen must be extremely thin for the subtle structural variations to be observable. As such, the sample thinning "window" for a successful sample is very small.

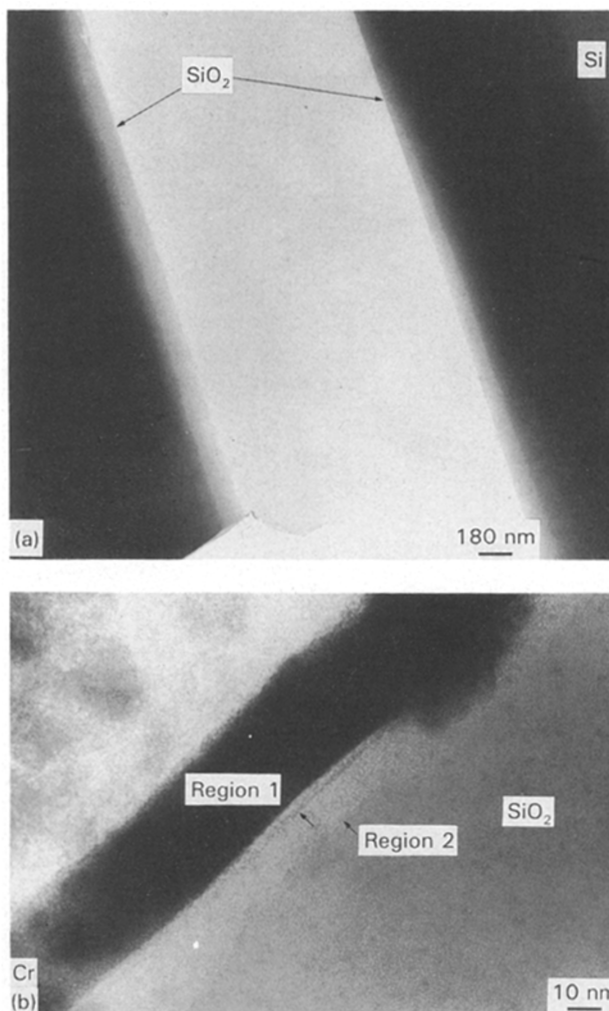


Figure 2 (a) Cross-sectional TEM micrograph of SiO_2 films having undergone more (left) and less (right) extensive polishing. (b) Cross-section of polished SiO_2 exhibiting two subsurface regions. The dark Cr film is necessary for sample preparation.

To expand this window a chromium film was deposited onto the surface of some polished oxide film specimens before sample preparation to protect the near-surface region and to prevent overthinning which resulted in the removal of the edge region.

As-deposited, annealed and polished specimens of each were examined using FTIR spectroscopy to identify overall structural changes occurring due to polishing. Films ranged from 1.5 μm to 150 nm in polished thickness and were examined for changes in silica network structure and hydration. The spectra in Fig. 3 corresponds to, from the top down, increasing polishing times for the films ranging from 2.0 to 1.5 μm in polished thickness, while those in Fig. 4 are from the films polished to the thicknesses indicated. The wavenumber range presented spans that of the primary silica structure peaks, which range from 450 to near 1250 cm^{-1}. The films that received an RTA were examined as-deposited, post-RTA and after polishing, their absorptive behaviours are shown in Figs 5 and 6.

3. Discussion

The TEM micrograph shown in Fig. 2a is from a sample produced from two films, the left having undergone a more extensive polishing process than the right, showing regions of lower density (as would occur due to hydration) through the phase contrast mechanism of TEM imaging. The regions extended to depths of 75–150 nm from the surface, corroborating the recent results in [4] on water absorption into a stressed silica surface at low temperatures. The CMP process resulted in hydration to a slightly greater depth, most likely due to the additional mechanical component involved.

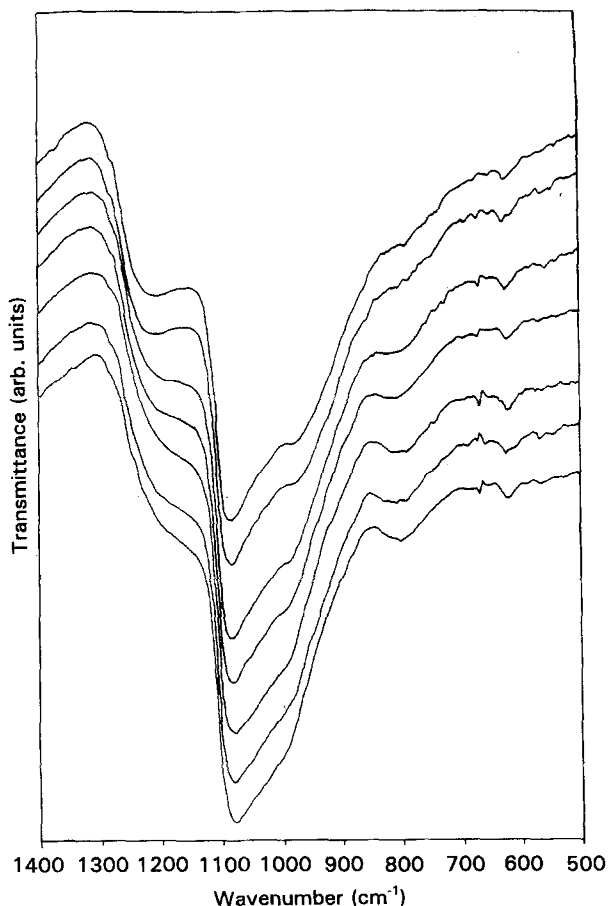


Figure 3 FTIR spectra corresponding to, from top down, decreasing final thickness (increasing polishing time) from 2.0–1.5 μm.

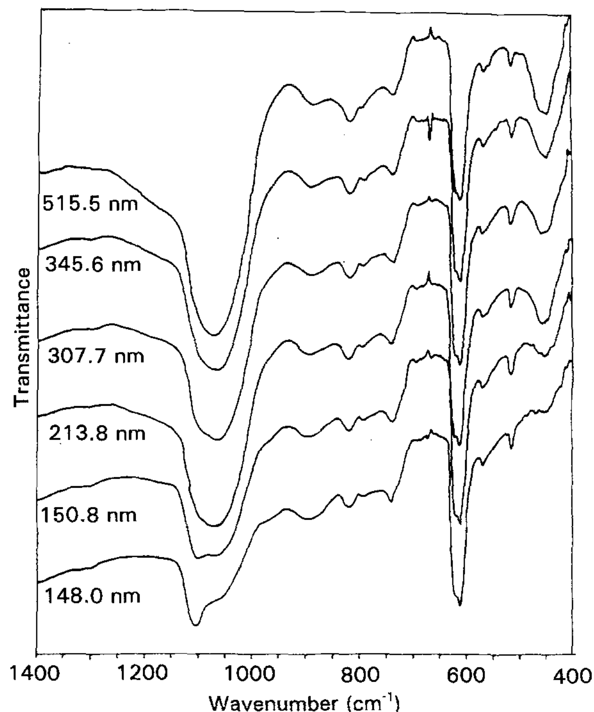


Figure 4 Transmittance spectra corresponding to films polished from an original thickness of 900 nm to the indicated thickness.

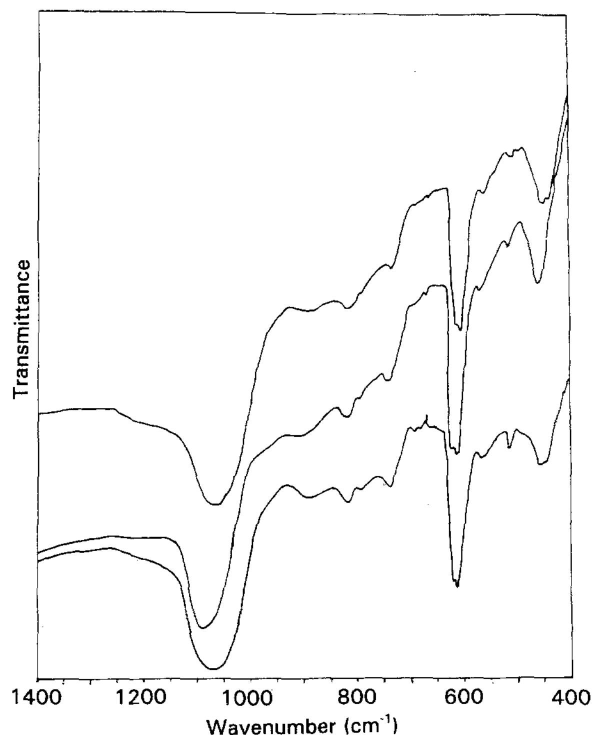


Figure 5 FTIR spectra from (top) as-deposited, (middle) rapid thermal annealed and (bottom) polished silica films.

The immediate near-surface region, examined in Fig. 2b, revealed two features: the first extended 3–4 nm below the surface, the second varied in depth from 15 to 20 nm. The locations and dimensions of these two distinct regions agree very accurately with

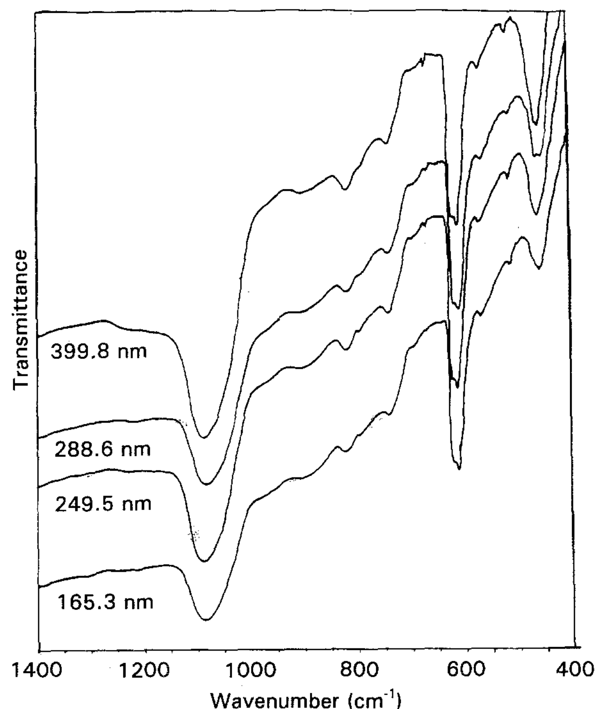


Figure 6 FTIR spectra of films that received a 1000 °C rapid thermal anneal before polishing to the indicated thickness.

those identified using grazing angle X-ray analysis in [5]. Note that the chemically altered and plastically deformed regions in Fig. 2b lie well within the region possessing an appreciable level of hydration in Fig. 2a.

The FTIR spectra contain the absorption peaks characteristic of Si–O–Si bonds in silicon dioxide at 450, 808 and 1070 cm^{-1}, as well as other features presently considered. In Fig. 3 the top spectrum, of the film undergoing the shortest polish, exhibits additional absorption peaks at 950 and 1200–1250 cm^{-1}. As polishing progressed, the peak at 808 cm^{-1} became more pronounced and the definition of spectrum "smeared" on both sides of the 1070 cm^{-1} peak to the 950 cm^{-1} peak on the low side and to the 1200–1250 cm^{-1} peak in the high side. Absorption near 950 cm^{-1} can be identified with two situations, the Si–OH stretch vibration and a component of a 1250/950 cm^{-1} band pair [6]. This pair represents a siloxane bridge with a significantly larger stretching force constant than the bulk corresponding to a highly strained or broken siloxane bond, possibly indicating a difference in Si atom coordination [7]. The contribution by the Si–OH vibrational mode is expected to be fairly small since the volume of the film in which hydration takes place is of the order of a few per cent, further reduced by the fact that only some of the siloxane bridges react, bringing the relative concentration of Si–OH bonds close to the detection resolution of the technique. The presence of the peak at 1200–1250 cm^{-1} suggests that the one at 950 cm^{-1} is primarily due to the band pair.

The smearing of the spectra between 1100 and 1250 cm^{-1} with increased polishing can be identified with two sources. FTIR analysis of very thin oxide films identified a strong absorption peak between 1150 and 1250 cm^{-1}, which was attributed to SiO_2 under high compressive stress [8]. In addition, a band pair cited at 1165 and 1200 cm^{-1} has been related to disorder within silica thin films [9]. Both of these are plausible as contributors to absorption in the 1100–1250 cm^{-1} range, given the nature of the CMP process and the potential reactions between the slurry and film.

The very thin films examined produced spectra with somewhat different character which, in addition to the characteristic absorption peaks at 450 and 1070 cm^{-1}, revealed other significant peaks. A strong peak occurring at 615 cm^{-1} is believed to be related to the silicon/oxide interface structure since it is observed in the spectra of substrates with native oxide as well as in both the transmission and reflection spectra of oxide films on silicon substrates; also it did not vary with polishing. The peak at 1107 cm^{-1}, emerging out of the fundamental silica peak as the film thinned and there were fewer bonds to absorb, may have been part of a band pair with the vibration corresponding to 815 cm^{-1}. This 1107/815 cm^{-1} band pair corresponded to a Si—O—Si bond angle of 145° (the equilibrium bond angle being ~ 150°), which agrees with the average bond angle in the interface region determined in modelling studies of the Si/SiO_2 interface [10], suggesting that these, as well, are due to the interface. These peaks are not generally observed in thicker films due to the larger scale at which the spectra are observed and the Rayleigh scattering noise from the film thickness, large when compared to the less than 1 nm thick strain layer at the interface. The shoulder on the high side of the fundamental silica stretch mode peak previously discussed and attributed to disorder and high strain in the network was also observed in these films.

Rapid thermal annealing of the oxide films before CMP processing resulted in an approximately 3% densification of the films and different spectral behaviour. Fig. 5 compares the spectra of as-deposited and polished films from both the RTA and unannealed groups, the final film thickness being almost the same, 249.5 and 213.8 nm, respectively. Most noticeable in the annealed films was the shift in the fundamental peak from 1070 to 1090 cm^{-1} and sharpening of the peak, corresponding to the narrowing distribution of vibrational modes of the Si–O–Si stretch. In addition, the annealed film exhibited a less pronounced high-side shoulder on the fundamental peak and greater absorption in general with increasing wavenumber, most likely due to the densification of the silica. The spectra of the annealed films varied little throughout polishing (see Fig. 6) suggesting a greater resistance to structural change induced by polishing. It is interesting to note that the absorption peak revealed at 1107 cm^{-1} in the unannealed sample as the film was thinned was not present in the annealed films.

4. Conclusions

The i.r. absorptive behaviour of as-deposited and annealed deposited silicon dioxide films that have undergone a chemical/mechanical polishing (CMP) planarization process has been investigated, resulting

in the following conclusions:

1. cross-sectional transmission electron microscopy of polished silica has revealed the presence of two near-surface regions, extending to 3 and 15–20 nm from the polished surface;
2. the location and depths of these regions correspond very accurately to those identified by other techniques as having significant structural alteration due to polishing;
3. FTIR spectroscopy has shown that polishing of the as-deposited films results in a broadening of the Si–O–Si fundamental peak and the development of other spectral features that can be associated with a highly strained, broken or disordered network, with possible loss of Si atom tetrahedral coordination;
4. polishing to very thin films maintains similar behaviour and, primarily due to the scale change, reveals other spectral features attributed to the Si/SiO_2 interface structure that were not present in the annealed films;
5. spectra from the annealed films exhibited changes resulting from structural rearrangements associated with densification;
6. polishing of the annealed films resulted in no changes in the i.r. spectra other than those resulting from the reducing interaction volume of the thinned films, suggesting that annealing the films increased their resistance to modification by the CMP process.

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