Temperature effect on low-k dielectric thin films studied by ERDA

2008 J. Phys.: Conf. Ser. 100 012041

(http://iopscience.iop.org/1742-6596/100/1/012041)

Temperature effect on low-k dielectric thin films studied by ERDA

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Abstract. Low-k dielectric materials are becoming increasingly interesting as alternative to SiO_2 with device geometries shrinking beyond the 65 nm technology node. At elevated temperatures hydrogen migration becomes an important degradation mechanism for conductivity breakdown in semiconductor devices. The possibility of hydrogen release during the fabrication process is, therefore, of great interest in the understanding of device reliability. In this study, various low-k dielectric films were subjected to thermal annealing at temperatures that are generally used for device fabrication. Elastic recoil detection analysis (ERDA) was used to investigate compositional changes and hydrogen redistribution in thin films of plasma-enhanced tetraethylortho-silicate (PETEOS), phosphorus doped silicon glass (PSG), silicon nitride (SiN) and silicon oxynitride (SiON). Except for an initial hydrogen release from the surface region in films of PETEOS and PSG, the results indicate that the elemental composition of the films was stable for at least 2 hours at 450°C.

1. Introduction

Silicon dioxide (SiO_2) has for several decades been the principal insulator in semiconductor devices. As the semiconductor industry has been shrinking transistor size in silicon-based integrated circuits (ICs) to achieve higher packing density, interlayer dielectric (ILD) has become one of the limiting factors in process integration and device performance. As device geometries are shrinking beyond the 65 nm node, it has become apparent to utilize a new generation of materials with much lower dielectric constant than SiO_2. Such low dielectric constant (low-k) materials are required to meet requirements for electrical performance of on-chip wiring [1-10].

Several thin films synthesized by various chemical vapor deposition (CVD) methods have been investigated to replace SiO_2. The properties of the synthesized films can be tuned to optimum performance by different process conditions. An important property of the new ILD is the thermal stability, because the processing conditions call for temperatures of 400 to 450 °C, which recently has generated great interests to study the thermal stability of low-k dielectrics.

Another important feature is the so-called negative bias temperature instability (NBTI) [11], which is mainly responsible for the conductivity breakdown due to the heat generated in the device, and main degradation mechanism of concern. High concentration of bound hydrogen is normally present in CVD dielectric films. The migration of hydrogen at elevated temperatures is thought to be one of the causes for shift in device threshold voltage, and first-principles calculations indicate that NBTI is due to the depassivation of Si-H bonds by protons that are trapped in complexes with dopants in the Si substrate [12]. As the hydrogen retention ability

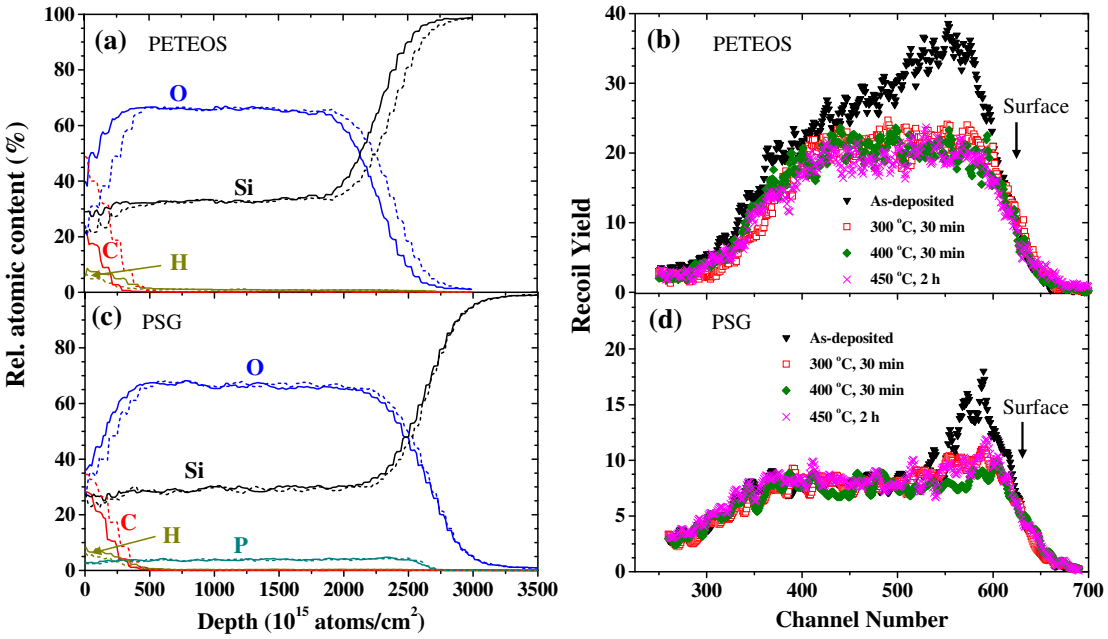

Figure 1. (a) Depth profiles of the relative atomic content obtained from ToF-E ERDA measurements of PETEOS (plasma-enhanced tetraethylortho-silicate) films before and after annealing for 2 hours at 450°C (full line: before annealing; dotted line: after annealing). (b) Hydrogen profile in the as-deposited PETEOS film and films that were subjected to thermal treatment at temperatures of 300 and 400°C for 30 min and a film heated to 450°C for 2 hours. (c) Same as (a) for PSG (phosphosilicate glass) films. (d) Same as (b) for PSG films.

varies between various low-k dielectric films, the possibility of hydrogen release during each of the fabrication process is of great interest to the study for the device reliability and degradation caused by NBTI.

In the present work we have studied the compositional stability to heat treatments of different low-k materials, such as PETEOS (plasma-enhanced tetraethylortho-silicate), PSG (phosphosilicate glass), SiN (silicon nitride), and SiON (silicon oxynitride). The compositional changes and hydrogen stability of the annealed dielectric films were in this study investigated by elastic recoil detection analysis (ERDA). Time-of-flight energy (ToF-E) ERDA [13] is ideally suited for the analysis of low-k materials containing light elements (H, C, N, and O) in addition to Si. The technique has sufficient mass resolution to detect these elements background free in contrast to Rutherford backscattering spectrometry [13]. However, special care should be taken for the analysis of hydrogen as the detector efficiency is often lower than 100% [14]. For hydrogen profiling conventional ERDA is more suitable [13].

2. Experimental

Thin films of PETEOS, PSG, SiN, and SiON were grown by CVD on silicon substrates. Samples were subjected to thermal annealing in a N_2 ambient atmosphere at temperatures up to 450 °C for a maximum of 2 hours. After cooling the samples down to room temperature, the elemental composition profiles were measured.

Elemental depth profiles of the thin films were measured using ToF-E ERDA with 45 MeV $^{127}I^{9+}$ ions as projectiles. The incident angle of primary ions and exit angle of recoils were both 67.5° to the sample surface normal giving a recoil angle of 45°. A detailed description of the experimental set-up has been given elsewhere [14]. All recoil ToF-E ERDA spectra were analyzed using the CONTES code [15] for extracting the depth profiles of relative elemental concentration.

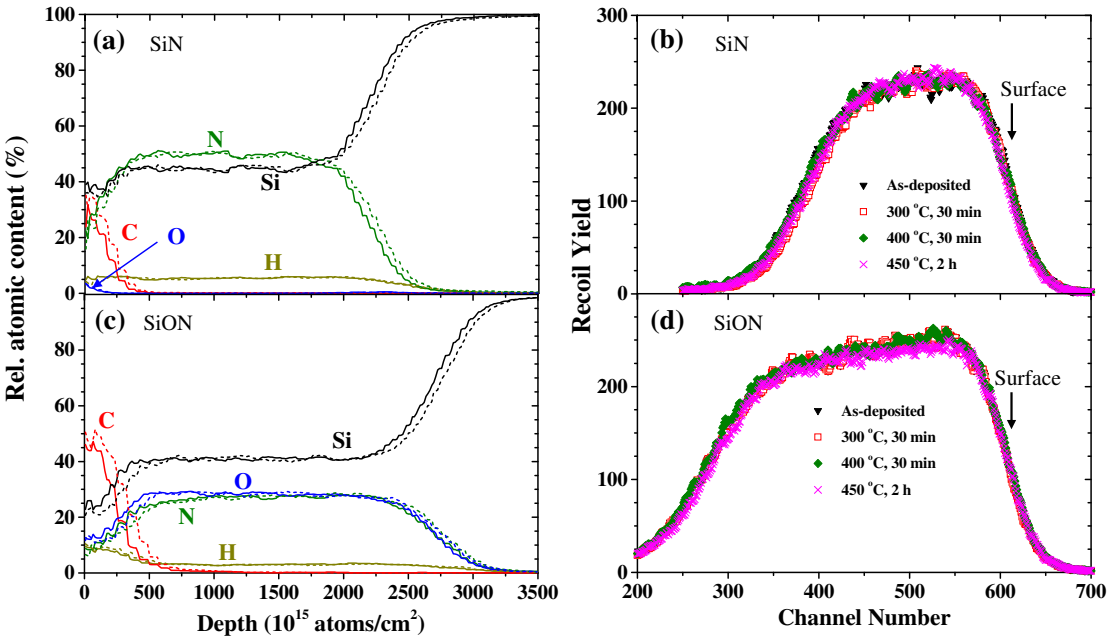

Figure 2. (a) and (b) same as Fig. 1 for SiN (silicon nitride). (c) and (d) same as Fig. 1 for SiON (silicon oxynitride).

The hydrogen distribution was measured by conventional ERDA measurements using 2.4 MeV He^+ ions as primary beam. An absorbing aluminium foil with a thickness of 10 μm was used in front of a surface barrier detector to filter out He^+ ions scattered from heavier elements. The incident angle of primary ions and exit angle of recoils were both 75° to the sample surface normal giving a recoil angle of 30°. The collected charge for a given sample was the same, making a comparison of the hydrogen content possible. Both ion beam analysis were carried out under high vacuum ($\sim 10^{-7}$ mbar) in the target chamber.

3. Results and Discussion

The ERDA results for the PETEOS and PSG films are shown in Fig. 1. The PETEOS films have a composition, which is very similar to SiO_2, Fig. 1(a). PETEOS films have been used as ILD to achieve better step coverage, especially for sub-μm gap spaces. The addition of phosphorus dopants during deposition results in a PSG film. This film becomes viscous at elevated temperatures, which is useful in forming uniform doping inside gaps with high aspect ratio. The composition of the PSG film appears to be mainly SiO_2 with a ~4% P doping, Fig. 1(c). In the bulk of both the as-deposited PETEOS and PSG films, there is a carbon content of ~0.2%, whereas the amount at the surface is much higher due to hydrocarbon contamination. The H concentration in the near surface region of both films consists of hydrogen from the films and from hydrocarbon contamination at the film surfaces.

After annealing at 300°C a significant lower H concentration is observed in the surface regions in both kind of films, see Figs. 1(b) and (d). Although the PETEOS films show some H reduction in the bulk of the film after this annealing, reduction of H is less significant in the bulk of the PSG films, indicating the existence of weakly bound hydrogen compounds in the bulk of the PETEOS films, compared to PSG. After annealing at 400°C, no significant H reduction is observed in both films, and H is more uniformly distributed in the films, ~7.5% in PETEOS films and ~2.5% in PSG films. Even after heat treatments at 450°C for 2 hours, the hydrogen profile is not changed essentially. The main composition of both films are preserved, as shown in Figs. 1(a) and (c). The ToF-ERDA data indicate a slight increase near the surface of the carbon content in the PETEOS and PSG films, whereas the bulk content is unchanged. The hydrogen loss at the

surface region may be attributed to the loss of water from the surface.

The ERDA measurements of the studied SiN and SiON films are shown in Fig. 2. Silicon nitride (SiN) is a widely used dielectric material in Very Large Scale Integration (VLSI) fabrication due to its impermeability to most impurities. The composition of the as-deposited SiN film seems to be stoichiometric, Fig. 2(a). Silicon oxynitride (SiON) have demonstrated improve stability and better cracking resistance with low film stress and are thus considered unique materials for ILD and final passivation layers. Our as-deposited SiON film has more silicon compared to nitrogen and oxygen, Fig. 2(c). Again carbon is seen at the surfaces of both films, and also some oxygen is seen at the surface of the SiN films due to hydrocarbon contamination. The carbon content in the bulk of the films is again $\sim$0.2%. However, the initial hydrogen content in SiN and SiON was much higher than in PETEOS and PSG. Even though ToF-ERDA has a low detection efficiciency for hydrogen a relative large amount was measured as seen in Fig. 2(a) and (c).

The heat treatments indicate that the SiN and SiON films are thermally stable up to 2 hours at 450°C. There is no essential change in the elemental composition measured by ToF-ERDA beside a slight increase in carbon contamination at the surface, Fig 2(a) and (c). Also there is no obsevable H loss or redistribution within the measurement uncertainties of ERDA, see Figs. 2 (b) and (d). This points towards strongly bound hydrogen in these materials.

4. Conclusions

The compositional stability has been investigated of PETEOS, PSG, SiN and SiON low-k dielectric thin films subjected to heat treatment at temperatures up to 450°C for a maximum of 2 hours. The results obtained by ERDA indicate that except for an initial hydrogen release from the surface region of the PETEOS and PSG films, the studied materials are stable at temperatures typically used at processing conditions for device fabrication.

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