

Suppression of hydrogen-ion drift into underlying layers using plasma deposited silicon oxynitride film during high-density plasma chemical vapor deposition

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Abstract

Hydrogen ions drifting into underlying layers during HDP-CVD were successfully suppressed by the insertion of plasma deposited silicon oxynitride ($p\text{-SiO}_x\text{N}_y\text{H}_z$) film, and the hydrogen-trapping mechanism was clarified. The hydrogen ions are trapped in bonding states, not in interstitial ones. After HDP-CVD undoped silicate glass (HDP-USG) film deposition on the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film, the decrease of the dangling bonds in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film measured by ESR was much lower than the increase of the desorbed hydrogen concentration measured by TDS. These results suggest that new hydrogen-trapping sites are mainly generated from ESR-inactive bonds by drifted hydrogen ions and atomic hydrogen during HDP-CVD.

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1. Introduction

Hydrogen in semiconductor devices such as ultra large scale-integrated (ULSI) circuit devices plays important roles for device performance and reliability, because hydrogen can terminate the defects in silicon, gate oxide and so on. However, hydrogen in ULSI devices often degrades its performance and reliability. Especially, hydrogen in the plasma deposited silicon nitride ($p\text{-SiN}$) film for passivation causes hot carrier degradation [1,2], negative bias temperature instability (NBTI) [3], threshold-voltage instability [4] and so on, because this film contains a large amount of hydrogen atoms and ions, and they can easily diffuse into the gate oxides. In order to suppress the hydrogen diffusion from the $p\text{-SiN}$ film, the successful insertion of a plasma deposited silicon oxynitride ($p\text{-SiO}_x\text{N}_y\text{H}_z$) film under the $p\text{-SiN}$ has been applied. Although the dangling bonds in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film play an important role for hydrogen trapping [5], the thermal stability of trapped hydrogen and the

hydrogen-trapping mechanism in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film has not yet been clarified. Furthermore, the thermal stability of the trapped hydrogen is important, because the fabricated semiconductor devices are often annealed and tested at high temperature.

Recently, another hydrogen-related issue has been reported: Hydrogen-ion drift into underlying layers by radio frequency (RF) bias [6], as shown in Fig. 1. During the gap-fill process by high-density plasma chemical vapor deposition (HDP-CVD) for inter-metal layer deposition, hydrogen ions dissociated from SiH_4 are accelerated by RF bias and implanted into the underlying layers. Then, the implanted hydrogen ions drift into the silicon substrate due to the inner electric field in the underlying layers, and some of them reach the gate oxides. These drifted hydrogen ions also degrade the transistor performance and its reliability. Compared to the diffusion process from the $p\text{-SiN}$ film, this electrical drifting process seems to be more serious, because the penetration depth and amount of drifted hydrogen are much larger than those of diffused hydrogen. In order to suppress these drifted hydrogen ions, a $p\text{-SiO}_x\text{N}_y\text{H}_z$ film is the first candidate for the hydrogen-stopping layer, because this film can suppress the hydrogen diffusion from the $p\text{-SiN}$ film.

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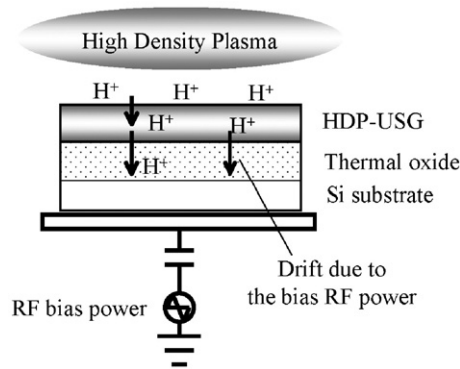


Fig. 1. Schematic of hydrogen-ion drift into the underlying thermal oxide during HDP-CVD.

In this paper, we report the suppression of hydrogen-ion drift into the underlying layers by the insertion of $p\text{-SiO}_x\text{N}_y\text{H}_z$ film during HDP-CVD using secondary ion mass spectroscopy (SIMS). Furthermore, the details of the hydrogen-trapping mechanism in $p\text{-SiO}_x\text{N}_y\text{H}_z$ film, such as the stability of trapped hydrogen and trapping sites, are investigated using thermal desorption spectroscopy (TDS) and electro-spin resonance (ESR) spectroscopy. Finally, the generation of new hydrogen-trapping sites and a feasibility model for its formation process are proposed.

2. Experimental

The $p\text{-SiO}_x\text{N}_y\text{H}_z$ films were deposited by conventional plasma-enhanced chemical vapor deposition (PECVD). The PECVD apparatus was parallel-plate type and 13.56 MHz-RF power was applied to the upper electrode. The precursors were SiH_4 and N_2O , and were supplied by the upper electrode. The temperature of the wafer stage and the deposition pressure were 400 °C and 200 Pa, respectively. The composition of the film was 36 at.% silicon, 40 at.% oxygen, 12 at.% nitrogen and 12 at.% hydrogen.

Two groups of samples were prepared; the purpose of the first group is evaluation for suppression of hydrogen-ion drift using the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film, and that of the second one is investigation into the details of the hydrogen-trapping mechanism, such as the stability of the trapped hydrogen and the presence of new hydrogen-trapping sites in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film. The first group of samples was prepared as follows: Three film-stacked structures were fabricated, as shown in Fig. 2. First, 100 nm-thick thermal oxides were grown on Si(100) substrates as underlying layers. Since the hydrogen concentration in thermal oxides is quite low, hydrogen depth profiles after HDP-CVD can be evaluated properly. Next, for Sample-A, a 500 nm-thick HDP-USG film was deposited. For Sample-B, a 200 nm-thick $p\text{-SiO}_x\text{N}_y\text{H}_z$ film deposition was followed by a 500 nm-thick HDP-USG film deposition. For Sample-C, only the 200 nm-thick $p\text{-SiO}_x\text{N}_y\text{H}_z$ film was deposited. The HDP-USG film was deposited by an HDP-CVD apparatus with inductively-coupled plasma source and RF bias using a $\text{SiH}_4\text{--O}_2\text{--Ar}$ system. In order to suppress the hydrogen diffusion during HDP-CVD, the deposition temperature was maintained

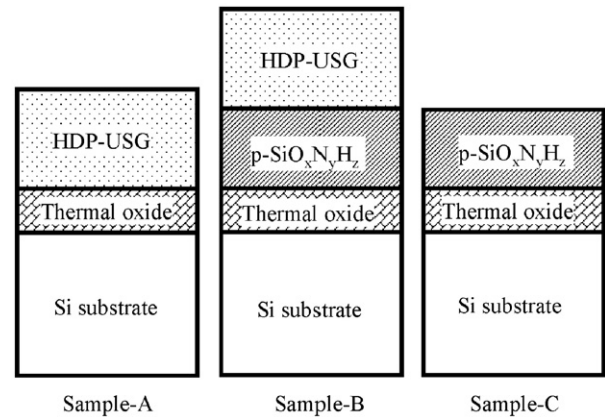


Fig. 2. Film stacks of Sample-A, Sample-B and Sample-C.

at a low 290 °C. The hydrogen depth profiles were evaluated by SIMS. A 10 keV Cs^+ primary-ion beam with current density of 0.3 $\mu\text{A}/\text{cm}^2$ was used for this measurement.

The second group of samples was prepared as follows: Fig. 3 shows the sample-fabrication procedure. For Sample-D, an 850 nm-thick $p\text{-SiO}_x\text{N}_y\text{H}_z$ film deposition on the Si(100) substrate was followed by a 500 nm-thick HDP-USG film deposition. Then, only the HDP-USG film was removed by buffered HF solution. After this process, the residual thickness was precisely controlled so as to equal the initial thickness of the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film. For Sample-E (control sample), only the 850 nm-thick $p\text{-SiO}_x\text{N}_y\text{H}_z$ film was deposited and its surface was slightly etched by the same solution to eliminate the effect of residual buffered HF on the surface in TDS measurement. The stability of the trapped hydrogen in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film during HDP-CVD was investigated by the TDS. The heating rate and the temperature range were 60 °C/min and 50 °C/1000 °C, respectively. The amount of desorbed hydrogen was normalized by a unit area of 1 cm^2 using sample weights. The quadruple mass sensitivity was calibrated by a hydrogen-doped silicon wafer whose dose amount was precisely controlled at 1×10^{16} atoms/ cm^2 . Using these calibrations, the accuracy of the hydrogen concentration measured by TDS was estimated to be $\pm 3\%$. The dangling-bond densities in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film were measured by ESR. The microwave power and the modulation width were 0.1 W and 0.1 mT, respectively.

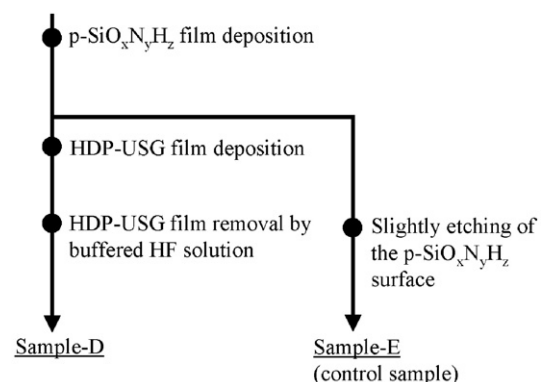


Fig. 3. Process flows of Sample-D and Sample-E.

3. Results and discussion

3.1. Suppression of hydrogen-ion drift into underlying layers using a $p\text{-SiO}_x\text{N}_y\text{H}_z$ film during HDP-CVD

First, we demonstrate the suppression effect of hydrogen-ion drift on the insertion of $p\text{-SiO}_x\text{N}_y\text{H}_z$ film. Fig. 4 shows the hydrogen depth profiles of Sample-A and Sample-B using SIMS. The zero position of “Depth” (horizontal axis) is the thermal oxides/silicon substrates interface. The depth profiles of the hydrogen concentrations in thermal oxides can be divided into three zones, Zone-1: a rapidly decreasing concentration adjacent to the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film/thermal oxide interface in the depth range of 50 to 100 nm, Zone-2: a concentration of bulk thermal oxide in the depth range of 20 to 50 nm, Zone-3: a peak at the thermal oxide/silicon substrate interface. In Zone-1, it is difficult to measure the hydrogen concentrations, because the SIMS measurements were conducted from the surface side and an artificial tailing of the hydrogen profiles caused by an atomic knock-on process could not be avoided [7–10]. Because the resolution of the depth profile for the upper interfaces of the thermal oxides is degraded, the hydrogen concentrations in Zone-1 are ignored. In Zone-2, the hydrogen concentration of sample-B was much lower than that of sample-A, even though the hydrogen concentration in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film was much larger than that in the HDP-USG film. This result indicates that the hydrogen-ion drift into the underlying layers during HDP-CVD is effectively suppressed by the insertion of $p\text{-SiO}_x\text{N}_y\text{H}_z$ film. The difference of hydrogen concentration in Zone-2 between Samples-A and Sample-B is about 5×10^{19} atoms/cm³. Since untrapped hydrogen ions in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film have drifted into the thermal oxide, this difference should be coincident with the hydrogen concentration trapped in the $p\text{-SiO}_x\text{N}_y\text{H}_z$ film. In Zone-3, the hydrogen concentration of Sample-B was much lower than that of Sample-A. Although it is quite difficult to estimate the concentration at these interfaces due to the sputter yield issue, this large difference is considered to be valid. Therefore, the insertion of $p\text{-SiO}_x\text{N}_y\text{H}_z$

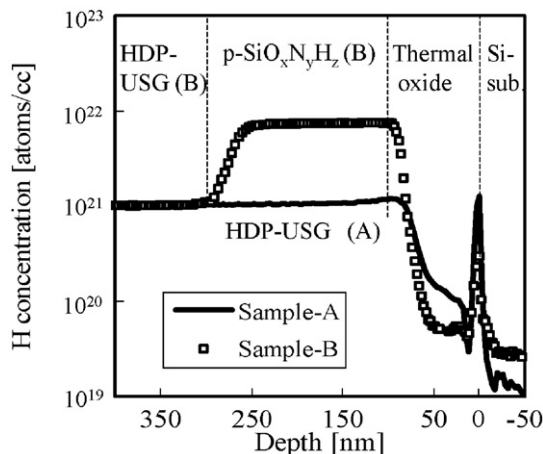


Fig. 4. Hydrogen depth profiles of Sample-A and Sample-B using SIMS. Sample-A: HDP-USG/thermal oxide/Si substrate. Sample-B: HDP-USG/ $p\text{-SiO}_x\text{N}_y\text{H}_z$ /thermal oxide/Si substrate.

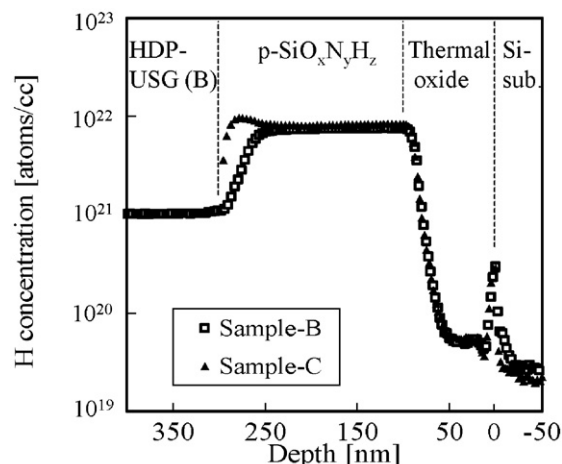


Fig. 5. Hydrogen depth profiles of Sample-B and Sample-C using SIMS. Sample-B: HDP-USG/ $p\text{-SiO}_x\text{N}_y\text{H}_z$ /Thermal oxide/Si substrate. Sample-C: $p\text{-SiO}_x\text{N}_y\text{H}_z$ /Thermal oxide/Si substrate.

film between thermal oxides and HDP-USG films effectively suppresses the hydrogen-ion drift into the thermal oxide and the thermal oxides/silicon substrate interface.

Next, we show the suppression capability of hydrogen-ion drift by the insertion of $p\text{-SiO}_x\text{N}_y\text{H}_z$ film during HDP-CVD. Fig. 5 shows the hydrogen depth profiles of Sample-B and Sample-C using SIMS. The depth profiles of Sample-B and Sample-C were almost the same for all zones. These results indicate that hydrogen-ion drift into underlying layers during HDP-CVD is completely suppressed by the insertion of $p\text{-SiO}_x\text{N}_y\text{H}_z$ film.

3.2. Hydrogen-trapping mechanism in $p\text{-SiO}_x\text{N}_y\text{H}_z$ film

In order to clarify the hydrogen-trapping mechanism in $p\text{-SiO}_x\text{N}_y\text{H}_z$ film, we investigated the stability of trapped hydrogen using TDS and the hydrogen-trapping sites in this film using TDS and ESR. Fig. 6 shows the TDS spectra of Sample-D and Sample-E below 500 °C. The hydrogen-desorption amount

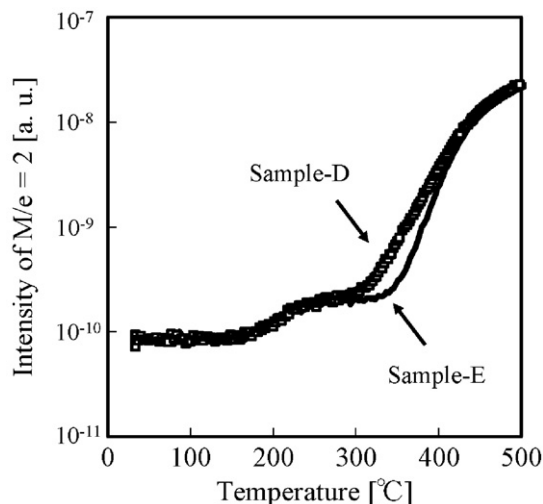


Fig. 6. TDS spectra of $p\text{-SiO}_x\text{N}_y\text{H}_z$ film.

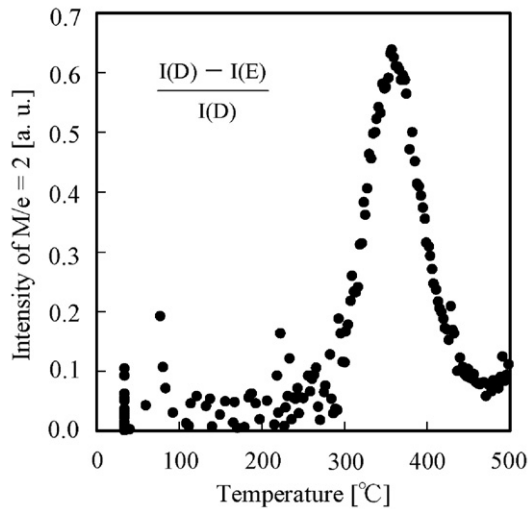


Fig. 7. Subtracted TDS spectrum normalized by spectrum of Sample-D.

For Sample-D was slightly larger than that for Sample-E in the temperature range of 300 °C to 400 °C. This difference is attributed to the concentration of trapped hydrogen after HDP-CVD. The increased concentration of desorbed hydrogen ions in p -SiO_xN_yH_z film was 1.08×10^{19} atoms/cm³. As mentioned in Section 3.1, the trapped hydrogen concentration in the p -SiO_xN_yH_z film after HDP-CVD measured by SIMS was estimated to be 5×10^{19} atoms/cm³. The difference is caused by the thermal stability of the trapped hydrogen. There are two kinds of bonding states in the trapped hydrogen, one is stable and the other is unstable. Therefore, 4×10^{19} atoms/cm³ hydrogen, the difference between the concentration measured by TDS and that measured by SIMS, is considered to be in stable states in the p -SiO_xN_yH_z film. Fig. 7 shows the desorbed spectrum obtained when that of Sample-E is subtracted from and then normalized by that of Sample-D. As shown in this figure, the subtracted spectrum has a peak at 360 °C. Considering the thermal stability of hydrogen in silicon [11–17], SiO₂ [18–20], SiN and so on, this result indicates that the hydrogen is trapped in the dangling bonds in p -SiO_xN_yH_z film such as Si–, Si=, O–, N=, not in interstitial sites.

In order to investigate the relationship between the concentration of trapped hydrogen and the densities of the dangling bonds in p -SiO_xN_yH_z film, the densities of the dangling bonds in

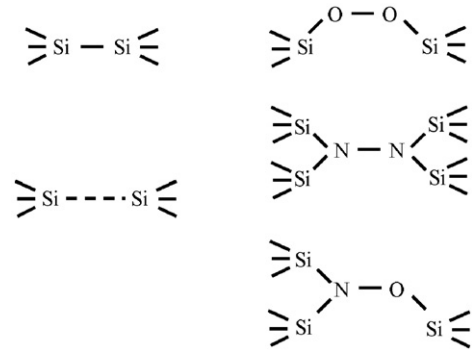


Fig. 8. Schematic of feasibility models of hydrogen-trapping sites in p -SiO_xN_yH_z film. Hydrogen ions might break ESR-inactive bonds and form H-terminated bonds [18–20].

the p -SiO_xN_yH_z film before and after HDP-CVD were measured by ESR. The results are shown in Table 1. Since the difference between the density of the dangling bonds in Sample-D and Sample-E is considered to be equal to the trapped hydrogen concentration, this difference should be coincident with the concentration of desorbed hydrogen measured by TDS. However, the difference of the dangling-bond densities measured by ESR (1.84×10^{18} spins/cm³) is much lower than the concentration of desorbed hydrogen measured by TDS (1.08×10^{19} atoms/cm³). These results indicate that other hydrogen-trapping sites are involved in hydrogen-trapping process during HDP-CVD. From this point of view, we propose a model of the bond breaking in p -SiO_xN_yH_z film during HDP-CVD. In this model, ESR-inactive bonds are broken and form new hydrogen-trapping sites.

Fig. 8 shows a schematic of the feasible atomic structures of ESR-inactive bonds in p -SiO $_x$ N $_y$ H $_z$ film [18–20]. As shown in this figure, ESR-inactive bonds such as Si–Si, O–O bonds or other weak bonds might be formed in as-deposited p -SiO $_x$ N $_y$ H $_z$ film. These bonds might be broken by two different processes during HDP-CVD. One is hydrogen-ion drift process and the other is ultraviolet (UV) light induced one. The hydrogen-ion drift process is as follows: Hydrogen ions generated by dissociation of SiH $_4$ are drifted by high electric field at plasma sheath and in p -SiO $_x$ N $_y$ H $_z$ film during HDP-CVD [6]. Then, hydrogen ions gain high momentum energy and internal one such as radical energy, and energies are high enough to break the ESR-inactive bonds in p -SiO $_x$ N $_y$ H $_z$ film. Finally, the broken ESR-inactive bonds might become new hydrogen-trapping sites. Simultaneously, these sites also trap hydrogen and form hydrogen-terminated bonds such as Si–H, O–H, N–H and their complexes.

The UV light induced process is as follows: Hydrogen molecules adsorbed at the surface are dissociated into atomic hydrogen by UV light generated by high-density plasma. Then, this atomic hydrogen breaks the ESR-inactive bonds and becomes new hydrogen-trapping sites during HDP-CVD [21,22].

4. Conclusion

The suppression of hydrogen-ion drift into underlying layers using p -SiO_xN_yH_z film during HDP-CVD, the stability of

Methodology	ESR	TDS
	Densities of dangling bonds (10^{18} spins/cm ³)	Concentration of desorbed hydrogen (10^{18} atoms/cm ³)
Sample-D	4.22	—
Sample-E	6.06	—
The difference of dangling bonds in Sample-D and Sample-E	1.84	—
Trapped hydrogen concentration	—	10.8

These are measured by ESR and TDS, respectively.

trapped hydrogen and the hydrogen-trapping sites in p -SiO_xN_yH_z film were investigated by SIMS, TDS and ESR. The inserted p -SiO_xN_yH_z film traps drifted hydrogen ions completely, and as a result, the hydrogen concentration in the underlying layer is drastically decreased. Hydrogen is trapped at dangling bonds, and might also be trapped at new trapping sites generated from defects in the p -SiO_xN_yH_z film. The bond breaking caused by hydrogen-ion drift or atomic hydrogen process might contribute to trap hydrogen in the p -SiO_xN_yH_z film during HDP-CVD.

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