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## Phosphorus ion implantation and POCI<sub>3</sub> doping effects of $n^+$ -polycrystalline-silicon/high-k gate dielectric (HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) films

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Phosphorus (P)-doped polycrystalline-silicon gate/HfO<sub>2</sub> or HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/p-type Si (100) metaloxide-semiconductor capacitors were fabricated using either a POCl<sub>3</sub> diffusion or an ion implantation technique to investigate the relationship between P penetration and the electrical properties of the high-k gate dielectric stacks. The  $HfO_2 - Al_2O_3$  bilayer showed higher P diffusion blocking properties as a result of the 4.1-nm-thick amorphous interface layer including  $Al_2O_3$  (or Al-silicate). The P ion-implanted sample with the  $HfO_2 - Al_2O_3$  bilayer sample had the smallest leakage current density of  $-8.8 \times 10^{-10}$  A/cm<sup>2</sup> at -1 V, which was due to the lower P penetration, and the higher trap depth of approximately  $1.3\pm0.02$  eV compared to  $0.9\pm0.02$  eV of the sample with only HfO<sub>2</sub>. However, the P doping by POCl<sub>3</sub> diffusion was too excessive and only very leaky devices were produced. © 2004 American Institute of Physics. [DOI: 10.1063/1.1697646]

For high-k gate dielectrics, the poly-Si gate electrode is still attractive due to its process maturity to industry and easy threshold voltage control<sup>1</sup> although the metal gate should eventually be used. However, dopant penetration from the poly-Si through the crystallized high-k gate dielectrics during high-temperature annealing results in unstable electrical characteristics. Quevedo-Lopez et al.<sup>2</sup> recently reported that phosphorus (P) penetrates through crystalline  $HfSi_rO_v$  into the Si substrate after rapid thermal annealing (RTA) at 1050 °C whereas P penetration was largely reduced when amorphous HfSi<sub>x</sub>O<sub>y</sub>N<sub>z</sub> films were used.

This study examined the P penetration behavior and electrical characteristics of the MOS capacitors with high-k gate dielectric stacks, POCl<sub>3</sub>-doped  $n^+$ -poly-Si gate/ HfO<sub>2</sub>/p-type Si (s1), POCl<sub>3</sub>-doped  $n^+$ -poly-Si gate/ HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/*p*-type Si (s2), P-ion-implanted  $n^+$ -poly-Si gate/HfO<sub>2</sub>/p-type Si (s3), and P-ion-implanted  $n^+$ -poly-Si gate/HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/p-type Si (s4) where the HfO<sub>2</sub> and  $Al_2O_3$  were grown by atomic layer deposition (ALD), were examined. An amorphous Al<sub>2</sub>O<sub>3</sub> layer was interposed between the HfO<sub>2</sub> film and the Si substrate to improve the P-diffusion blocking properties as has been performed for improving the As-diffusion blocking properties.<sup>3</sup> Doping by POCl<sub>3</sub> diffusion was attempted in order to investigate the dopant diffusion blocking capability of the HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> stack under extreme conditions.<sup>4</sup>

The MOS capacitors with HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films were fabricated on p-type epitaxial Si (100) wafers with a resistivity of 1  $\Omega$  cm (~1×10<sup>-17</sup> cm<sup>-3</sup>). The HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films were deposited by an ALD (Ever-tek. Co, Plus-200) technique on the standard Radio Corporation of America cleaned wafers using HfCl<sub>4</sub>, Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O as the precursors and oxidant for the HfO2 and Al2O3 films, respectively, at a wafer temperature of 300 °C. Postdeposition annealing of the samples was performed with RTA at 900 °C under a N<sub>2</sub> atmosphere for 30 s.  $n^+$ -poly-silicon gates were fabricated by depositing the 200 nm thick poly-Si layers at 625 °C on the high-k layers and ex situ doping the poly-Si layers using POCl<sub>3</sub> diffusion and ion-implantation techniques. The POCl<sub>3</sub> diffusion was performed at 900 °C for 14 min with a POCl<sub>3</sub> carrier gas flow rate of 400 sccm, and the films were annealed at 900 °C in situ for 20 min in the diffusion furnace. The P implantation was performed using an acceleration voltage of 50 keV with a P dose of 5  $\times 10^{15}$ /cm<sup>2</sup>. The P-implanted samples were dopant activation-annealed at 1000  $^\circ C$  under  $N_2$  for 20 s by RTA after the gate patterning. The high-k film thicknesses were measured by ellipsometry and cross-section high-resolution transmission electron microscopy (HRTEM). A low-energy secondary ion mass spectrometer (SIMS) using a Cs<sup>+</sup> primary ion source with an acceleration voltage of 3 keV was used to investigate the P-diffusion profiles.

The back side of the wafer was HF cleaned with Al metallization being subsequently applied for the electrical measurements. Postmetallization annealing was performed at 400 °C for 30 min under a 5%  $H_2$ +95%  $N_2$  atmosphere in order to stabilize the electrical properties. A HP4194A impedance meter and HP4155A semiconductor parameter analyzer were used to determine the capacitance versus voltage (C-V) at 1 MHz, and the leakage-current density versus voltage (J-V) measurements, respectively. The degree of dopant activation in the poly-Si was measured using a Hall analyzer (BIO-RAD HL5500).

Figures 1(a)-1(d) show HRTEM pictures of the s1, s2, s3, and s4 samples, respectively, after the whole fabrication process of the MOS capacitors. The HfO2 layers were crystallized for all samples, and they were already crystallized at the as-deposited states (TEM data not shown). Amorphous interfacial layers (ILs) at the interfaces between the  $HfO_2$ films and Si substrates of the s2 and s4 samples must be composed of  $Al_2O_3$ , Al silicate and interfacial  $SiO_{2-x}$ .<sup>5</sup> The

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FIG. 1. HRTEM results of (a) s1 (HfO<sub>2</sub>) and (b) s2 (HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) doped by POCl<sub>3</sub>. And, those of (c) s3 (HfO<sub>2</sub>) and (d) s4 (HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) doped by P-ion-implantation samples after RTA at 1000 °C 20 s.

estimated thickness of each layer from the HRTEM pictures are; *s*1: Top IL (1.3 nm)/HfO<sub>2</sub> (10.2 nm)/bottom IL (2.0 nm), total 13.5 nm, *s*2: Top IL (0.7 nm)/HfO<sub>2</sub> (8.3 nm)/Al<sub>2</sub>O<sub>3</sub> bottom IL (4.0 nm), total 13.0 nm, *s*3: Top IL (1.1 nm)/HfO<sub>2</sub> (10.7 nm)/bottom IL (1.7 nm), total 13.5 nm, and *s*4: Top IL (0.7 nm)/HfO<sub>2</sub> (8.3 nm)/Al<sub>2</sub>O<sub>3</sub> bottom IL (4.1 nm), total 13.1 nm. The total capacitance equivalent thicknesses (CET) estimated from the accumulation C-V data of *s*3 and *s*4 were approximately 4.6 and 4.8 nm, respectively, which corresponds to a total dielectric constant of 11.4 and 10.6, respectively. The *s*1 and *s*2 samples were too leaky to obtain saturated C-V curves in the accumulation region.

Figure 2(a) shows the P-diffusion profiles of the four samples measured by SIMS. It should be noted that the *s*3 and *s*4 were activation annealed by RTA at 1000 °C. It can be seen that the surface P-doping concentration (5.1  $\times 10^{21}$ /cm<sup>3</sup>) in the poly-Si layer as a result of POCl<sub>3</sub> diffusion was more than double that of the surface P-doping concentration (2.1 $\times 10^{21}$ /cm<sup>3</sup>) doped by the P implantation. The *s*2 and *s*4 sample show better P-diffusion blocking properties (steeper P profile in the Si substrate) compared to *s*1 and



FIG. 2. (a) The P-diffusion profiles of the four samples measured by SIMS after dopant activation RTA at 1000 °C 20 s, and (b) C–V plots of the samples measured at 1 MHz. Inset graph shows J-V curves.

s3 samples, respectively, which indicate that the rather thick (4.0–4.1 nm) amorphous layer of the sp2 and sp4 sample worked as an effective P-diffusion blocking layer. Although the crystalline HfO<sub>2</sub> layers have a relatively large thickness, a single HfO<sub>2</sub> layer cannot suppress P diffusion due to the presence of grain boundaries that act as the high-diffusivity path. The thin ILs of the s1 and s3 did not sufficiently work as P-diffusion blocking layers. The P peak concentration ( $\sim 3.3 \times 10^{22}$ /cm<sup>3</sup>) in the high-k gate dielectric and interfacial layer of the s1 and s2 shows approximately five times higher value than that ( $\sim 7 \times 10^{21}$ /cm<sup>3</sup>) of s3 and s4, which results in a larger leakage current of the s1 and s2 samples, as will be discussed later.

Because of the excessively high doping concentration of the poly-Si electrode, it is essential to estimate the activated P concentration of the samples in order to correctly understand the electrical characteristics, particularly the flat-band voltage  $(V_{\rm fb})$  and the fixed charge densities  $(Q_f)$ . The Hall measurements showed that s1 and s2 have an activated P concentration of  $6.24 \times 10^{20}$ /cm<sup>3</sup> (sheet resistance of 28 ohm/ sq.), and s3 and s4 have  $1.71 \times 10^{20}$ /cm<sup>3</sup> (127 ohm/sq.) in their poly-Si electrodes. These results show that only 12% and 8% of the doped P impurity were activated in the cases of POCl<sub>3</sub> diffusion and P implantation, respectively, under the given experimental conditions. The nonactivated P concentration of the s1 and s2 was 2.4 times higher than that of the s3 and s4, and the nonactivated P atoms mainly diffuse through the grain boundaries in the poly-Si and through the gate oxide into Si substrate, which can give rise to the high leakage current.<sup>6</sup>

Figure 2(b) shows the C-V plots of the s2, s3, and s4 samples measured at 1 MHz. The C-V curves of the s3 and s4 exhibit good saturation behaviors in the accumulation region as a result of the low leakage as shown in the inset. However, the C-V curve of s2 steeply increased in the accumulation region due to the high leakage current, and that of s1 could not be measured because of the very high leakage current density. Because of the heavy doping concentration of the poly-Si gate and P diffusion into the substrate, the active acceptor concentrations  $(N_a)$  of the Si substrates of each sample were estimated from the C-V plots. The  $N_a$ 's were  $6.27 \times 10^{16}$ ,  $6.99 \times 10^{16}$ , and  $8.04 \times 10^{16}$  for s2, s3, and s4, respectively. It can be understood that the P diffusion reduced the  $N_a$  of the substrates and the amount of reduction became smaller for the samples with the ion implantation and with the  $Al_2O_3$  IL, which is consistent with the SIMS results. The work functions  $(\psi_m)$  of the poly-Si electrodes can be estimated from the active P concentrations of each electrode, using the Fermi-Dirac distribution of the electrons. The ideal flat-band voltage  $(V_{\text{fb}}^i)$  of the MOSCAP devices is given as Eq. (1),<sup>7</sup>

$$V_{\rm fb}^{i} = \psi_{m} - (\chi + E_{g}/2 + 0.026 \ln(N_{a}/1.45 \times 10^{10})), \qquad (1)$$

where  $\chi$  and  $E_g$  are the electron affinity (4.05 eV) and energy band gap, respectively, of Si.

The calculated  $V_{fb}^i$  of s2, s3, and s4 using Eq. (1) are -1.132, -1.026, and -1.029 V, respectively, and the measured flat-band voltages from their respective C-V curve are 0.368, -0.922, and -0.151 V, respectively. Therefore, the final  $V_{fb}$  shifts are 1.50, 0.10, and 0.88 V for the s2, s3, and



FIG. 3. P–F plot of the current density of the s3 (HfO<sub>2</sub>) sample. The inset graph shows the Arrhenius plots of the s3 sample with various gate bias.

s4, respectively. The positive  $V_{\rm fb}$  shift values suggest that the high-k films have negative fixed charges, and their densities  $(N_f)$ , which were estimated using the CET values, are approximately  $7.5 \times 10^{12}$ ,  $4.7 \times 10^{11}$ , and  $4.0 \times 10^{12}$  cm<sup>-2</sup>, for the s2, s3, and s4, respectively. Here, the CET of s2 was roughly estimated from the capacitance value at -1.5 V. The high  $N_f$  values of the s2 and s4, compared to that of the s3, show that the Al<sub>2</sub>O<sub>3</sub> layers have a high density of negative fixed charges. This is consistent with previous reports.<sup>5,8</sup> The ALD HfO<sub>2</sub> layers usually have positive fixed charges on its own.<sup>9</sup> Therefore, the negative sign of fixed charges in the s3suggests that the  $N_f$  of s3 was induced by the P diffusion. Lee *et al.*<sup>10</sup> showed that the diffused P ions in  $SiO_2$  gate oxide behave as network modifiers and result in a negative  $Q_f$ .<sup>10</sup> It appears that the same mechanism works for these high-k films and P diffusion results in the formation of negative fixed charges. The comparatively small P diffusion in the cases of the ion-implanted samples, s3 and s4, induced a relatively small  $N_f$  formation. The approximately one order of magnitude smaller  $N_f$  of s3 compared to that of s4 suggests that the large  $N_f$  of s4 mainly results from the Al<sub>2</sub>O<sub>3</sub>. Indeed, the  $N_f$  of approximately  $4 \times 10^{12}$  cm<sup>-2</sup> from the Al<sub>2</sub>O<sub>3</sub> layer is well consistent with the author's previous estimation.<sup>11</sup> However, the higher P diffusion of the s2, as a result of  $POCl_3$  diffusion, results in a very high  $N_f$  in addition to the  $N_f$  formed by the Al<sub>2</sub>O<sub>3</sub> layer. The additional  $N_f$ induced by P diffusion for the case of s2 is approximately  $3.5 \times 10^{12}$  cm<sup>-2</sup>, which is quite high.

The inset figure of Fig. 2(b) shows the variations in the current density (*J*) as a function of the gate bias of the various samples. It can be observed that the excessive P diffusion of the *s*1 and *s*2 results in an unacceptably high *J* irrespective of the presence or absence of an Al<sub>2</sub>O<sub>3</sub> IL although the high-*k* film thicknesses were quite high (~13 nm). When the P diffusion was properly reduced (*s*3 and *s*4) the *J* is sufficiently small up to a very high voltage (-3 V), and the Al<sub>2</sub>O<sub>3</sub> IL further reduced the leakage current.

Figure 3 shows the Poole–Frenkel (P–F) plots of s3 of the *J* in the high-voltage (>2.7 V) region at various temperatures (25–150 °C). Here, the electric field was calculated by considering the fact that the film is composed of two layers (10.7 nm thick HfO<sub>2</sub> with a dielectric constant ( $\varepsilon_r$ ) of 20 and 1.7 nm thick SiO<sub>2</sub> with an  $\varepsilon_r$  of 4), and the field shown in the *x* axis is the field applied to the HfO<sub>2</sub> layer. From the slope and *y* intercept of the inset graphs, the  $\varepsilon_r$  and trap depth of

the HfO<sub>2</sub> layer were estimated to be approximately 3.5 and  $0.9\pm0.02$  eV, respectively. The estimated  $\varepsilon_r$  is consistent with the square of the refractive index of the film (1.8–1.9).

The same P-F analysis of the s4 was performed assuming that the dielectric film is composed of two layers with an 8.3 nm thick HfO<sub>2</sub> layer with a dielectric constant ( $\varepsilon_r$ ) of 19 and a 4.1 nm thick Al-silicate layer with an  $\varepsilon_r$  of 7.5. When the electric field of the  $HfO_2$  was taken as the x axis variable of the P–F plot, the estimated  $\varepsilon_r$  was far <2 suggesting that most of the electric field was applied to the rather thick Alsilicate IL. When the IL field was taken as the field for the P–F emission, the estimated  $\varepsilon_r$  and trap depth were approximately 3.7 and  $1.3\pm0.02$  eV, respectively. The estimated  $\varepsilon_r$ was slightly higher than that of the square of the refractive index of the  $Al_2O_3$  (~1.7), which might result from some error in estimating the static dielectric constants and the electric field. The deeper trap depth of the IL might originate from the wider band gap of the IL, and contributes to the smaller leakage current of s4.

In summary, this study examined the P-diffusion behavior and electrical characteristics of the POCl<sub>3</sub> diffusion or P-ion-implantation-doped  $n^+$ -poly-Si gate HfO<sub>2</sub> or HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/*p*-type Si (100). The excessive P doping from POCl<sub>3</sub> diffusion results in a very high leakage current that renders the device useless. The P-ion-implantation-doped  $n^+$ -poly-Si gate/HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> bilayer structure showed good P-diffusion blocking properties and the lowest leakage current due to the amorphous nature and deeper trap nature of the IL containing Al<sub>2</sub>O<sub>3</sub>. However, the high negative fixed charge density of the high-*k* stack is a problem that remains to be solved.

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