Evidence of recombination enhanced diffusion of impurities at low temperature into high-k dielectric with tantalum oxide as an example

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(Received 22 June 2009; accepted 4 December 2009; published online 23 February 2010)

For ordinary diffusion of Si into Ta$_2$O$_5$ on a Si substrate, there should be no difference for n-type or p-type substrate; however, experimentally, we noticed that Si can diffuse rapidly and this diffusion process tended to be faster for n-type Si substrate than for p-type Si substrate under an oxygen plasma at 350 °C. This can only be explained by the mechanism of recombination enhanced diffusion. Beside Si, B, and Sb were shown to be able to diffuse into tantalum oxide under an oxygen plasma or nitrous oxide plasma at a temperature below 400 °C. © 2010 American Institute of Physics. [doi:10.1063/1.3315871]

Recombination of electrons and holes in a semiconductor or insulator can release energy. Excess carriers can be generated by optical injection or electrical injection. The energy release by the recombination of excess electrons and holes can enhance defect diffusion in a semiconductor or insulator. This concept is known as recombination enhanced defect diffusion, which can occur at lower temperature than usual. Recently, high dielectric constant (high-k) metallic oxide films have attracted world-wide interest and tantalum oxide (Ta$_2$O$_5$) is one of them. Leakage current has to be greatly reduced for tantalum oxide to be useful and a Japanese research group attempted to use low temperature UV/O$_2$ or UV/O$_3$ annealing to reduce leakage current through Ta$_2$O$_5$ films on silicon. They observed that silicon can diffuse from the silicon substrate through the Ta$_2$O$_5$ film and form a silicon suboxide on top of the Ta$_2$O$_5$ film even at relatively low temperature below 400 °C but they did not give a physical explanation. Subsequently, silicon suboxide on top of the Ta$_2$O$_5$ film after a low temperature plasma annealing process was also observed by us. However, both the Japanese research group and our team did not give a physical explanation regarding the mechanism involved. In this letter, we would like to report our attempt to explain the phenomenon by the mechanism of “recombination enhanced diffusion of impurities through a high-k dielectric.”

For ordinary diffusion through a high-k dielectric, the diffusion coefficient $D$ is given by

$$D = K_0 \exp(-E_A/(kT)),$$

where $K_0$ is a constant and $E_A$ is the activation energy.

For recombination enhanced defect diffusion through a high-k dielectric, the diffusion coefficient $D$ is given by

$$D = K_{rec}(np)\exp(-E_{A,rec}/(kT)).$$

$K_{rec}$ is a constant, $n$ and $p$ are the concentration of electrons and holes in the high-k dielectric. $E_{A,rec}$ is the activation energy for recombination enhanced defect diffusion. In general, $E_{A,rec}$ is significantly smaller than $E_A$. $E_A-E_{A,rec}$ is usually quite big, but may not be as large as the energy band gap of the high-k dielectric; this can be explained that the recombination of electrons and holes may occur through some intermediate energy levels in the high-k dielectric by an indirect recombination process instead of a direct recombination process. Diffusion becomes faster through the mechanism of “recombination enhanced diffusion” because the energy barrier for barrier has been reduced by $E_A-E_{A,rec}$.

During optical illumination, electron hole pairs will be generated in the high-k dielectric. In addition, some electrons and holes will come from the Si substrate through internal photoemission into the high-k dielectric as shown in Fig. 1.

In addition, $n = n_{photo} + n_{from_Si}$. \hspace{1cm} (3)

Similarly, $p = P_{photo} + p_{from_Si}$. \hspace{1cm} (4)

Naturally, $p_{photo} = n_{photo}$. \hspace{1cm} (5)

However, it can be predicted that, for tantalum oxide,

$p_{from_Si} < n_{from_Si}$. \hspace{1cm} (6)
According to solid-state physics, an insulator is just like a large band gap semiconductor and so there are free electrons in the conduction band and free holes in the valence band just like a semiconductor; thus Ta$_2$O$_5$ can be treated like a semiconductor with a band gap of about 4.4 eV.¹⁰ Using Table I of the paper by Robertson,¹⁰ the conduction band offset between Ta$_2$O$_5$ and Si is as small as 0.3 eV while the valence band offset between Ta$_2$O$_5$ and Si can be estimated to be as large as 2.9 eV. We believe that light can generate electron hole pairs both in Ta$_2$O$_5$ and Si; evidence of optical generation in Ta$_2$O$_5$ can be found in various reports of photoconductivity.¹¹,¹² In addition, there is internal photomission from Si into Ta$_2$O$_5$. For Ta$_2$O$_5$/n$^+$-Si samples, electrons in n$^+$-Si can go to the conduction band of Ta$_2$O$_5$ more easily than holes in p$^+$-Si can go to the valence band of Ta$_2$O$_5$ by internal photomission, resulting in much stronger recombination enhanced diffusion in Ta$_2$O$_5$/n$^+$-Si samples than Ta$_2$O$_5$/p$^+$-Si samples. Indeed this was observed experimentally as follows.

Ta$_2$O$_5$ films were deposited onto n$^+$-Si (doped by Sb) or p$^+$-Si (doped by B) wafers by low-pressure metal-organic chemical vapor deposition as reported before.¹³ Tantalum ethoxide Ta$_2$(OC$_2$H$_5$)$_4$ diluted by nitrogen reacted with oxygen to deposit Ta$_2$O$_5$ films on Si substrates. For this study, the deposition temperature was 430 °C and the deposition rate was 1.12 nm per minute; the Ta$_2$O$_5$ film thickness was about 15 nm. The plasma annealing was performed in a commercial plasma enhanced chemical vapor deposition (PECVD) chamber. For this work, the samples were annealed by O$_2$ or N$_2$O plasma annealing at 350 °C for 30 min.; attention should be paid to the fact that the annealing temperature was 80 °C below the deposition temperature. The pressure was 0.45 Torr. The rf (13.56 MHz) power used was 100 W. Secondary ion mass spectrometry (SIMS) was used for impurity depth profiling. We believe that our low temperature O$_2$ or N$_2$O plasma annealing process is similar to low temperature UV/O$_2$ or UV/O$_3$ annealing reported by other workers in terms of the presence of “light;” we believe that the light generated by the plasma can have a similar effect like the ultraviolet light used by other workers in terms of the creation of a silicon suboxide on top of the tantalum oxide film. Cross-sectional transmission electron microscopy (XTEM) was performed to detect any silicon suboxide formed by the O$_2$ or N$_2$O plasma annealing process. Electron diffraction experiments have been done to confirm that the Ta$_2$O$_5$ film is amorphous before and after low temperature plasma annealing.

For Ta$_2$O$_5$ as deposited on silicon, XTEM shows that there is no silicon suboxide on top of it as seen in Fig. 2(a). Only after low temperature O$_2$ or N$_2$O plasma annealing, a silicon suboxide film can be easily observed by XTEM. Figure 2(b) shows a schematic drawing of the Ta$_2$O$_5$/Si sample after low temperature plasma annealing and special attention should be paid to the SiO$_x$ film on top of Ta$_2$O$_5$. From XTEM pictures as shown in Figs. 2(c) and 2(d), it can be easily seen that the SiO$_x$ film on top of Ta$_2$O$_5$/n$^+$-Si is thicker than that on top of Ta$_2$O$_5$/p$^+$-Si as predicted by our theory discussed above.

Si distribution of the SIMS results shown in Figs. 3(a) and 3(b) for Ta$_2$O$_5$/p$^+$-Si and Ta$_2$O$_5$/n$^+$-Si samples also showed that Si atoms can diffuse into the Ta$_2$O$_5$ films during plasma annealing. This effect is significantly stronger for O$_2$ plasma annealing than for N$_2$O plasma annealing for both Ta$_2$O$_5$/p$^+$-Si and Ta$_2$O$_5$/n$^+$-Si samples. An interesting point observed from all these SIMS results was that the Ta$_2$O$_5$/Si interface was shifted in the plasma annealed samples from that of the as-deposited sample. This shift was more obvious in the O$_2$ plasma annealed samples than in the N$_2$O annealed samples. An explanation for this was that a SiO$_x$ layer actually formed on top of the Ta$_2$O$_5$ film during plasma annealing. It can be easily observed from SIMS results that this SiO$_x$ layer is thicker for a Ta$_2$O$_5$/n$^+$-Si sample compared to a Ta$_2$O$_5$/p$^+$-Si after O$_2$ plasma annealing. All of these experimental observations can be explained by our suggestion that light generated by the plasma annealing process can produce a large quantity of electrons and holes in the high-k
dielectric and the recombination of electrons and holes can enhance diffusion of impurities (for example, silicon) through a high-k dielectric.

Besides Si, a similar effect should occur for other impurities. The dopant distributions as seen from the SIMS results shown in Figs. 4(a) and 4(b) for Ta$_2$O$_5$/p$^+$-Si and Ta$_2$O$_5$/n$^+$-Si samples, showed that there was diffusion of dopants B and Sb from the silicon substrate into Ta$_2$O$_5$ films during plasma annealing even though the temperature was as low as 350 °C. Antimony (Sb) is usually difficult to diffuse even at high temperature because of its size; however, Sb diffusion can be easily observed in Ta$_2$O$_5$/n$^+$-Si samples after O$_2$ plasma annealing. Our explanation is that this is due to the light generated during plasma annealing which can enhance the dopant diffusion by the recombination enhanced diffusion mechanism. This diffusion was somewhat more obvious in O$_2$ plasma annealed samples than that of N$_2$O plasma annealed samples.

In conclusion, we propose that recombination enhanced diffusion of impurities into high-k dielectric by optical injection can be a low temperature mechanism of impurity entering high-k dielectric. The deposition of the Ta$_2$O$_5$ film on Si was done at 430 °C and XTEM shows that there is no silicon suboxide film on top of the Ta$_2$O$_5$ film; however, a silicon suboxide film can be easily observed by XTEM after plasma annealing at 350 °C, which is 80 °C below the deposition temperature of 430 °C. Similarly, SIMS shows that there is no serious Si diffusion at the deposition temperature of 430 °C but fast Si diffusion occurs during plasma annealing at 350 °C. This is an indication that the fast diffusion of Si across the Ta$_2$O$_5$ film is not due to conventional thermal diffusion. Hence, our experimental results show that impurities can diffuse into a high-k dielectric like tantalum oxide. In addition, O$_2$ plasma is significantly stronger than N$_2$O plasma in terms of capability to enhance impurity diffusion. If the impurities diffuse by a simple thermal mechanism, there should be no difference at all between O$_2$ plasma and N$_2$O plasma. In general, Sb is an impurity with low diffusion coefficient even at high temperature because of its big atomic size. We managed to show that Sb can diffuse into Ta$_2$O$_5$ at just 350 °C because of recombination enhanced diffusion. By the way, Ta$_2$O$_5$ films are amorphous in the as-deposited state and after low temperature plasma annealing and so there is no enhanced diffusion due to grain boundary effects. Electrically, the effect of recombination enhanced diffusion of silicon through Ta$_2$O$_5$ can be seen as a decrease in capacitance after plasma annealing because of the formation of the extra SiO$_x$ layer on top; this decrease in capacitance is stronger for O$_2$ plasma compared to N$_2$O plasma. In addition, there is an extra effect as follows. Tanimoto et al. reported that the leakage current of tantalum oxide on silicon capacitors first decreased with UV/O$_3$ annealing time; however, when the annealing time was long, a reverse effect was observed as shown in their Fig. 7. This is probably a sign of Ta$_2$O$_5$ contamination due to recombination enhanced diffusion from the silicon substrate. We observed that the leakage current of an Al/Ta$_2$O$_5$/n$^+$-Si capacitor with N$_2$O plasma annealing for 60 min. decreased at relatively high bias voltage but increased obviously at relatively low bias voltage compared to a similar capacitor with N$_2$O plasma annealing for 30 min. Our explanation is that the decrease of the leakage current at high bias voltage is due to the suppression of oxygen vacancies and the removal of carbon impurities; the increase of the thickness of the SiO$_x$ layer may also have some contribution. The increase of leakage current at low bias voltage is probably due to silicon contamination resulting from recombination enhanced diffusion from the silicon substrate. Similar observation was also made for O$_2$ plasma annealing but the effect was less obvious. As discussed by us before, the oxygen vacancy is a deep double donor but silicon can form a much shallower single donor by complexing with the oxygen vacancy; furthermore, the silicon oxygen vacancy complex is even shallower than the carbon oxygen vacancy complex. Thus the mechanism of recombination enhanced diffusion in high-k dielectrics can be used to explain some old mysterious effects reported before. Recently, recombination enhanced diffusion was also reported for insulators like diamond or magnesium oxide.

We would like to acknowledge the help of Ms. Peizhen Yang and Mr. T.T. Sheng. In addition, we would like to thank Dr. Taejoon Han and Mr. Neal Sandler for supply of samples.