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Lau, Wai Shing.

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Mechanism of Difficulty to Study the Physics of Leakage Current Reduction by Nitridation of Silicon before High-k Dielectric Deposition due to Change in Nucleation Characteristics and Some Other Factors

W.S. Lau

Nanyang Technological University (Retired)

School of EEE, Nanyang Avenue, Singapore 639798, Singapore

Abstract

It is expected that the leakage current can be reduced by nitridation of silicon before high-k dielectric deposition. In reality, it is not so simple because the nucleation of high-k dielectric on nitrated silicon may be different from the nucleation on silicon. In addition, the interfacial layer between the high-k dielectric becomes thinner because of the nitridation. Furthermore, the bandgap of the interfacial layer becomes smaller due to the nitridation. However, there may be less defect states in the high-k dielectric because of the nitridation. More in-depth study is needed to clarify whether leakage current is really reduced by nitridation. Experimental observation indicates the leakage current can be increased or decreased by nitridation depending on the details of the processing conditions. However, the capacitance is usually increased by nitridation; reduction of capacitance due to RTN is an unusual observation but it is possible.

Introduction

When a very thin high-k metallic oxide dielectric film is deposited on silicon, there may be chemical reaction between the high-k dielectric film and silicon with the possibility of the possibility of forming an interfacial layer of silicon oxide with a much lower dielectric constant, resulting in a lower overall capacitance. In addition, there may be an increase in leakage current due to an increase in oxygen vacancies due to the chemical reduction of high-k metallic oxide dielectric film by silicon. Furthermore, silicon may diffuse into the high-k dielectric film resulting in silicon contamination. It is expected that the overall capacitance can be increased by nitridation of silicon before high-k dielectric deposition because silicon nitride has a larger dielectric constant compared to silicon dioxide. Historically, the first report on the application of nitridation of silicon before high-k deposition is probably the work by Kamiyama et al.; Kamiyama et al. reported their experimental results on tantalum oxide capacitors on silicon with rapid thermal nitridation (RTN) done before tantalum oxide deposition (1). The improvement in capacitance due to RTN can be seen by a decrease in SiO₂ equivalent thickness, as shown in their Fig. 5.

It is also expected that the leakage current can be reduced by nitridation of silicon before high-k dielectric deposition. In reality, it is not so simple. The improvement in leakage current by RTN is not obvious in the report by Kamiyama et al. (1). In their Fig. 8, the leakage current was plotted against equivalent field, which is the voltage divided by SiO₂ equivalent thickness, instead of the bias voltage; Kamiyama et al. tried to claim that there is an improvement in leakage current according to their Fig. 8. Thus it is not obvious by reading the report of Kamiyama et al. to order to find out whether the current-voltage (I-V) characteristics were improved by RTN or not. In this paper, the author used tantalum oxide as an example just like Kamiyama et al. (1). Experimentally, the leakage current was sometimes observed to be reduced by nitridation of silicon before deposition; however, the opposite case could also be experimentally observed. The author would like to point out that both cases can be understood as follows.

Experimental

Ta₂O₅ was deposited onto (100) n⁺-Si substrates by low-pressure metal-organic chemical vapor deposition (LP-MOCVD) as discussed before (2). The physical thickness of the film was from 8-100 nm. As deposited Ta₂O₅ films tend to be very leaky and a post-deposition anneal is necessary to reduce the leakage current. Post-deposition anneal of Ta₂O₅ samples was done by RTP (rapid thermal processing) in O₂ or N₂O at 700-900°C. Al top contacts were deposited by electron beam evaporation. Zero-bias thermally stimulated current (ZBTSC) spectroscopy measurements were performed for the characterization of defect states at a ramp rate of 0.5 K/s as before (2). Rapid thermal nitridation (RTN) was sometimes performed on silicon substrates at 950°C in an ammonia ambient at atmospheric pressure. Capacitance-voltage (C-V) measurement was done at 1 kHz with the help of a lock-in amplifier. A relatively low frequency of 1 kHz was used because the capacitance was high and there would be less problem due to series resistance at 1 kHz. C-V measurement at 1 kHz shows up typical high frequency type of C-V characteristics with significantly less problem due to series resistance effects (3).

Results and Discussion

The author observed that the nucleation of tantalum oxide deposited by chemical vapor deposition (CVD) on silicon with native oxide and on nitrided silicon is different. The nucleation of CVD tantalum oxide tends to be more difficult on nitrided silicon than on silicon with native oxide, resulting in thinner film deposited on nitrided silicon than on silicon with native oxide. Cross-sectional transmission electron microscopy (XTEM) confirmed that the tantalum oxide film deposited on nitrided silicon is thinner than that deposited on silicon. This can be seen in Table I; the thickness of as deposited CVD tantalum oxide is reduced from 8 nm to 7.33 nm due to RTN. It is known that silicon nitride has difficulty of nucleation on silicon dioxide because the silicon nitride/silicon dioxide pair is non-wetting (4). It is known that silicon nitride has difficulty of nucleation on silicon dioxide but not on silicon nitride (5). It can be guessed that the silicon nitride/tantalum oxide pair is also non-wetting such that tantalum oxide may have some difficulty of nucleation on nitrided silicon. Liu et al. pointed out that tantalum oxide deposited by CVD on Pt is slower than on PtO (6). Thus the deposition process can be sensitive to the nature of the surface of the substrate.

In addition, nitridation of silicon makes the silicon more difficult to be oxidized than silicon with native oxide. This can be also seen in Table I; the thickness of the interfacial layer is smaller for sample with RTN. Furthermore the bandgap of silicon nitride and silicon oxynitride is smaller than that of silicon dioxide. All these factors tend to make the leakage current higher for tantalum oxide on nitride silicon compared to tantalum oxide on silicon with native oxide.

However, nitridation may reduce the defect states in tantalum oxide. Reduction of tantalum oxide by silicon can generate oxygen vacancies. Nitridation helps to block this reaction. This factor tends to make the leakage current smaller. Some idea regarding whether defect states can be reduced by nitridation can be obtained by the zero-bias thermally stimulated current (ZBTSC) spectroscopy technique.

Table I The thicknesses of the Ta₂O₅ layer and the interfacial layer in the capacitor structures with and without RTN after RTA in O₂ from XTEM analysis

		Capacitors before RTA	Capacitors after RTA at 700 °C in O ₂ for 30s	Capacitors after RTA at 750 °C in O ₂ for 30s	Capacitors after RTA at 800 °C in O ₂ for 30s	Capacitors after RTA at 800 °C in O ₂ for 10s
Capacitor with RTN	Ta ₂ O ₅ layer thickness	7.33 nm	6.67 nm	6.0 nm	5.33 nm	7.33 nm
	Interfacial layer thickness	0.67 nm	2.00 nm	2.67 nm	2.67 nm	2.00 nm
Capacitor without RTN	Ta ₂ O ₅ layer thickness	8.00 nm	7.33 nm	7.33 nm	6.00 nm	7.33 nm
	Interfacial layer thickness	1.33 nm	2.67 nm	2.33 nm	3.00 nm	2.67 nm

Fig. 1 I-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without nitridation of silicon before deposition after RTA in O₂ for 10 s at 800°C before Al deposition. The leakage current is significantly increased due to RTN. Diameter = 1 mm.

Fig. 2 C-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without nitridation of silicon before deposition after RTA in O₂ for 10 s at 800°C before Al deposition. The capacitance is significantly increased due to RTN. Diameter = 1 mm.

Fig. 3 shows the ZBTSC spectra of Al/Ta₂O₅/n⁺-Si capacitor with and without rapid thermal nitridation (RTN) of silicon before deposition for a particular set of 2 samples. It can be seen by Fig. 1 that defect states can really be reduced by RTN. Fig. 4 shows the I-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without RTN for the same set of 2 samples. It can be seen by Fig. 4 that leakage current can really be reduced by RTN for both positive voltage and negative voltage applied to the Al gate. Fig. 5 shows the C-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without RTN for the same set of 2 samples. Fig. 5 shows that the capacitance is significantly increased by RTN.

Fig. 3 ZBTSC spectra of Al/Ta₂O₅/n⁺-Si capacitor with and without nitridation of silicon before deposition. Diameter = 1 mm.

Fig. 4 I-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without nitridation of silicon before deposition: (a) Al gate positively biased and (b) Al gate negatively biased. Diameter = 1 mm.

Fig. 5 C-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without nitridation of silicon before deposition after RTP in O₂ at 800°C for 30 s. Diameter = 1 mm.

Secondary ion mass spectrometry (SIMS) was also used to study the effect of RTN on silicon diffusion into the tantalum oxide film. It is a surprise that the reduction of silicon contamination by RTN is not obvious according to SIMS. However, from the SIMS measurement, it was observed that the tantalum oxide film deposited on nitrated silicon is significantly thinner than that deposited on silicon.

By concentrating on a particular set of 2 samples, it can be found that the leakage current is reduced by RTN and the tantalum oxide film with RTN is actually thinner. In this way, it can be solidly concluded that RTN can really reduce defect states in tantalum oxide, resulting in leakage current reduction. It is not so difficult to see that under some situations, the reduction in film thickness due to change of nucleation characteristics by RTN is the dominant effect, resulting in an “apparent” increase of leakage current by RTN. It is not so difficult to imagine that silicon nitride and other high-k dielectric may also be non-wetting such that this work can serve as a reference for other high-k dielectric materials.

Fig. 6 C-V characteristics of Al/Ta₂O₅/n⁺-Si capacitor with and without nitridation of silicon before deposition after RTP in N₂O at 800°C for 30 s. Diameter = 1 mm.

In general, the capacitance for samples with RTN is higher than that for samples without RTN. This is because silicon nitride has larger dielectric constant compared to silicon dioxide. In addition, silicon nitride inhibits oxidation because it is an oxygen diffusion barrier. However, the author observed that sometimes an unusual experimental observation that the capacitance for samples with RTN is smaller than that for samples without RTN was made, as shown in Fig. 6. The author's explanation for this unusual observation is that without RTN the interfacial oxide is undergoing two opposing effects simultaneously when Ta₂O₅/Si is heated in an oxidizing ambient: (A) interfacial oxide growth and (B) interfacial oxide thinning because of silicon monoxide (SiO) sublimation (7). RTN can inhibit interfacial oxide growth. RTN can also inhibit interfacial oxide thinning because of silicon monoxide (SiO) sublimation. Under some situations, the latter is the stronger effect, resulting in an unusual experimental observation that the capacitance for samples with RTN can be smaller than that for samples without RTN. As shown in Table I for the sample without RTN undergoing RTP in O₂ for 30 s, the interfacial layer thickness is thicker after RTP in O₂ at 700°C for 30 s compared to the as-deposited sample. However, the interfacial layer thickness is thinner after RTP in O₂ at 750°C for 30 s compared to the sample after RTP in O₂ at 700°C for 30 s. When the RTP is further increased to 800°C, the interfacial layer becomes thicker again. Thus the interfacial layer thickness as a function of RTP temperature has a minimum at 750°C. This was explained to be due to SiO sublimation before (7).

Similar observation can be seen in Table II for the sample without RTN undergoing RTP in N₂O for 30 s. SiO sublimation observation was quite frequently done in an ultra-high vacuum (UHV) environment (8-9). This may create an impression that SiO sublimation only happens in UHV. Actually SiO sublimation can also happen at atmospheric pressure (7). GeO sublimation at GeO₂/Ge interface has been observed at atmospheric pressure (10). GeO is more volatile than SiO and so GeO sublimation can be observed more easily than SiO sublimation. With sufficient care, SiO sublimation can also be observed at atmospheric pressure (7).

Conclusion

In conclusion, nitridation of silicon before high-k deposition may or may not decrease leakage current. However, nitridation of silicon before high-k deposition usually increases the capacitance. Decrease of capacitance due to nitridation of silicon is a rare observation but it is possible.

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Table II: the Ta₂O₅ layer and the interfacial layer thickness in the capacitors with and without RTN after RTA in N₂O from XTEM analysis.

		Capacitors before RTA	Capacitors after RTA at 700 °C in N ₂ O for 30s	Capacitors after RTA at 750 °C in N ₂ O for 30s	Capacitors after RTA at 800 °C in N ₂ O for 30s	Capacitors after RTA at 800 °C in N ₂ O for 10s
Capacitor with RTN	Ta ₂ O ₅ layer thickness	7.33 nm	7.33 nm	7.00 nm	6.67 nm	7.33 nm
	Interfacial layer thickness	0.67 nm	3.00 nm	3.67 nm	4.00 nm	2.67 nm
Capacitor without RTN	Ta ₂ O ₅ layer thickness	8.00 nm	8.00 nm	7.67 nm	6.00 nm	8.00 nm
	Interfacial layer thickness	1.33 nm	3.33 nm	2.67 nm	3.67 nm	1.67 nm

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