

Study of tungsten oxidation in O₂/H₂/N₂ downstream plasma

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The surface oxidation of tungsten is a serious issue in plasma processing of advanced integrated-circuit devices where tungsten is being used as a gate electrode. In this article, we study tungsten oxidation in O₂/H₂/N₂ downstream plasma at a temperature ≤ 300 °C. The results show that oxidation occurs rapidly in O₂ downstream plasma to form stable WO₃. However, oxidation can be reduced effectively by adding H₂ and totally suppressed when H₂ concentration in the gas feed reaches a certain low level at which the plasma is still oxygen dominant. Tungsten oxidation increases significantly with sample temperature and exposure time in O₂ downstream plasma. However, H₂ addition reduces both temperature and time dependences due to the coexistence and competition of oxidation and reduction processes. When N₂ is also added, the efficiency of H₂ in O₂ downstream plasma in controlling tungsten oxidation is lowered. The findings may provide effective approaches to various applications of selective oxidation over tungsten, such as photoresist stripping and polysilicon oxidation on tungsten gate structures. © 2008 American Vacuum Society.

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I. INTRODUCTION

As the device feature size of integrated circuits (ICs) continues to be scaled down, a metal or polysilicon/metal stack has been used to replace polysilicon as a gate electrode for transistor formation to lower sheet resistance and increase device speed. Among different metals investigated, tungsten meets various electrical and process requirements and has gradually been adopted for ≤ 45 nm nodes.¹ However, tungsten can be oxidized easily when exposed to oxygen plasma during processing,^{2,3} leading to degradation of device performance. One example is postimplantation or postetch photoresist (PR) stripping in oxygen plasma, where tungsten oxidation results in gate critical-dimension change or poor electrical contact. Although an effective approach to solve this problem is available by using an oxygen-free reducing gas,² such chemistry usually gives a very low PR removal rate and poor process uniformity. The second example is selective oxidation of polysilicon over tungsten in the polysilicon/tungsten gate stack after gate etching to anneal etching damage where tungsten oxidation is difficult to prevent with the presence of oxygen. The current common approach is using water vapor and hydrogen mixture to do thermal oxidation,⁴ but the process requires very high temperature and tends to cause contamination issue. These two examples represent some major challenges in advanced IC device fabrication involving metal gate structures. Either new chemistry or a new process approach is urgently needed to provide solutions to existing problems.

Although thermal oxidation of tungsten in oxygen and other gases has been investigated extensively,⁵ only a few studies on tungsten oxidation in oxygen plasma are available.^{2,3,6} Furthermore, detailed information about the behavior of tungsten oxidation in plasmas of gas mixtures is still not available. In this article, we present a study on tung-

sten oxidation in a downstream plasma reactor using an O₂, H₂, and N₂ mixture. For the two application examples mentioned above, our experimental result provides a good solution for PR removal over the tungsten gate; it also enhances a new approach for polysilicon oxidation on the tungsten/polysilicon gate stack at low temperature.⁷ In general, the methodology could be implemented for other applications where selective control of tungsten oxidation is required.

II. EXPERIMENT

This work was performed in a Suprema downstream plasma chamber from Mattson Technology. As shown in Fig. 1, there are two portions inside the chamber separated by a grid with small holes. A plasma is generated by a 13.56 MHz power source of 2500 W applied to an inductive coil around a quartz cylinder in the upper portion. Downstream plasma with reactive free radicals is obtained in the lower portion as ionic species are quenched by the grid. The test sample sits on a pedestal and its temperature is controlled by the pedestal temperature set by a heater. The chamber is evacuated by a dry mechanical pump. Process gases are introduced through a nozzle at the top of the chamber at designated flow rates. Chamber pressure is maintained at 800 mtorr during the test with a throttle valve.

The tungsten samples are blanket tungsten films of 100 Å thick prepared by chemical vapor deposition on silicon oxide wafers. The oxidation of the tungsten surface is examined by x-ray photoelectron spectroscopy (XPS). The XPS spectra are obtained from a PHI Quantum 2000 spectrometer with Al K α radiation at 1487 eV as the excitation source. The film thickness of the tungsten and the oxide grown on the surface are measured using an ultraviolet ellipsometer on a Nanometrics 8300X system before and after the oxidation tests, and the differences are obtained as tungsten loss and oxide growth, respectively. Because the tungsten measurement has been found to be more consistent and reliable during differ-

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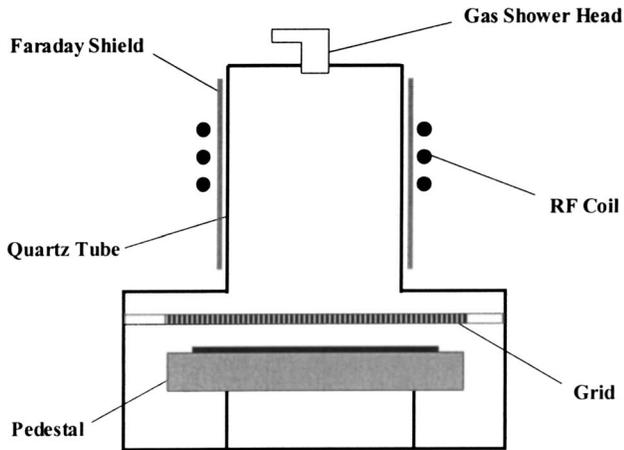


FIG. 1. Schematic diagram of Suprema downstream plasma reactor.

ent tests, tungsten loss data are used in the following discussion. In addition to the work on tungsten oxidation, two other sets of tests have also been done for potential applications. One is PR stripping on tungsten, where blanket I-line PR wafers are used to obtain a PR strip rate. The second application is selective oxidation of polysilicon over tungsten, where *p*-type (100) single-crystalline Si wafers are used to grow thin oxide. The film-thickness measurement for both PR and SiO_2 are also done using the Nanometrics system.

III. RESULTS AND DISCUSSION

Figure 2 shows the $W(4f)$ XPS spectra of the tungsten samples before and after exposing them to the O_2 downstream plasma at a pedestal temperature of $300^\circ C$. Based on deconvolution analysis, the spectra of the tungsten surface before oxidation contain a strong signal contributed by W^0 , with $W(4f_{7/2})$ and $W(4f_{5/2})$ peaks corresponding to two electron spin states located at 31.2 and 33.4 eV, respectively. Two similar peaks at 35.6 and 37.8 eV can also be seen, but are weaker in intensity. These two peaks correspond to W^{+6} in the form of WO_3 . After being oxidized for 120 s, the XPS intensity is almost totally shifted from W^0 to W^{+6} . For both cases, the signals from W^{+4} and other components correlated to WO_x ($x \leq 2$) are very weak. These results indicate that the tungsten surface is oxidized strongly after being exposed to the oxygen downstream plasma, and the stable tungsten oxide is WO_3 .

The extent of tungsten oxidation is measured by tungsten loss using ellipsometry. The result of oxidation in O_2 and O_2/H_2 downstream plasmas at $300^\circ C$ is given in Fig. 3. The tungsten loss is as large as 14 \AA in pure O_2 plasma (equivalent to $\sim 35 \text{ \AA}$ oxide growth), but decreases rapidly when H_2 is added. When the H_2 percentage in the gas feed reaches about 15%, the tungsten loss is reduced to zero, which means no more oxidation beyond the initial state. Since in such a small H_2 concentration, oxygen radical density does not decrease significantly, the dramatic reduction in tungsten oxidation is caused by surface reactions. When more H_2 is added, the tungsten loss becomes negative, indicating tungsten film growth. The negative loss or growth is due to the

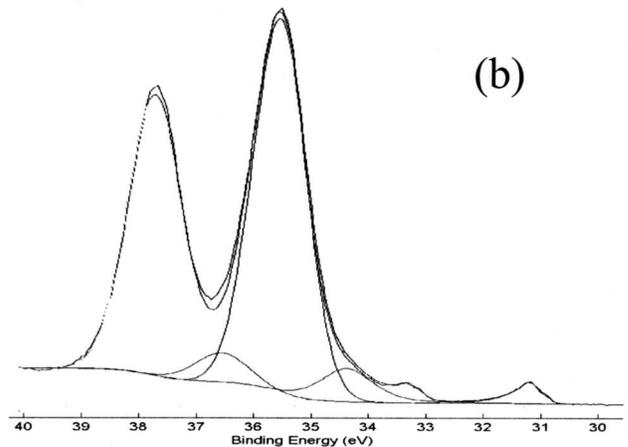
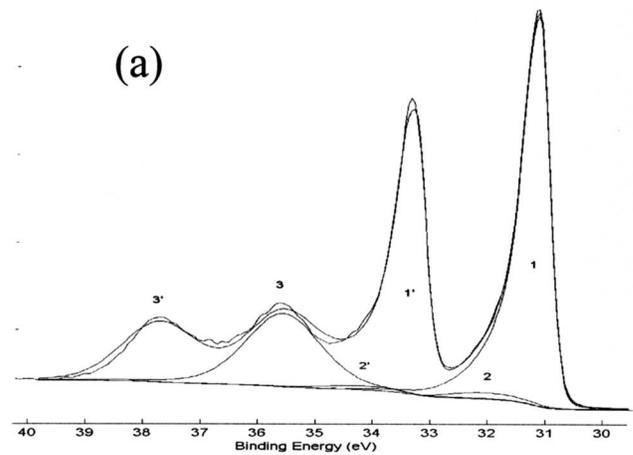


FIG. 2. XPS spectra of tungsten surface (a) before and (b) after oxidation in O_2 downstream plasma. Plasma exposure time = 120 s.

reduction of the native tungsten oxide by the hydrogen species to tungsten. Based on this result, the H_2 level for zero loss is quite low and the chemical environment is still oxy-

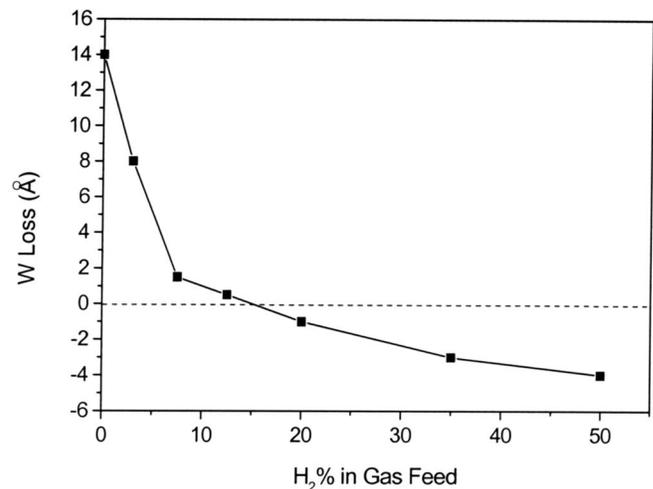


FIG. 3. Tungsten loss as a function of $H_2\%$ in O_2/H_2 downstream plasmas. Plasma exposure time = 120 s.

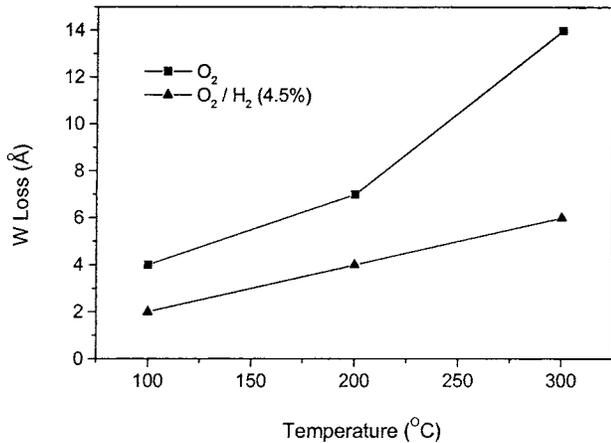


FIG. 4. Tungsten loss as a function of wafer temperature. Plasma exposure time=120 s.

gen rich. Therefore, the use of O₂/H₂ in a downstream plasma actually shows that tungsten oxidation can be suppressed while other simultaneous requirements—such as high PR strip rate or selective oxidation of polysilicon in the previous two examples—can be met.

In downstream plasma, the sample temperature usually is a dominant factor in controlling process results due to the lack of ion bombardment to accelerate surface reactions. This is also true for the current case of tungsten oxidation. As shown in Fig. 4, a higher pedestal temperature enhances oxidation and causes more tungsten loss. When the wafer is heated from 100 to 300 °C in pure O₂ plasma, the tungsten loss increases significantly from about 4 to 14 Å. The increase shows an exponential trend, so more rapid oxidation is expected at even higher temperature. When H₂ is added into the plasma, however, the oxidation behavior changes significantly in two aspects, as seen in the figure for the case of 5% H₂ addition. First, the tungsten loss becomes less at any fixed temperature. Second, the temperature dependence becomes more linear, which means that more effective reduction of oxidation can be achieved at higher temperature. This behavior change with temperature from pure O₂ to O₂/H₂ mixture also indicates the coexistence of competing, but kinetically different, oxidation and reduction reactions on the tungsten surface. Although the detailed reaction mechanism and parameters for these two reactions are not clear, we expect that the activation energy for the oxidation is lower than that for reduction, leading to the slowdown of oxidation with increasing temperature.

Figure 5 shows another unique characteristics of tungsten oxidation control in O₂/H₂ downstream plasma. When pure O₂ is used, we found that the tungsten loss due to oxidation increases quite linearly with time, probably caused by continuous diffusion of oxygen through the tungsten oxide on the surface into the bulk tungsten. However, after adding enough hydrogen to pass the zero-loss level, the tungsten oxide thickness basically remains unchanged after about 60 s from the beginning. This means that an equilibrium state between oxidation and reduction has been reached. Obvi-

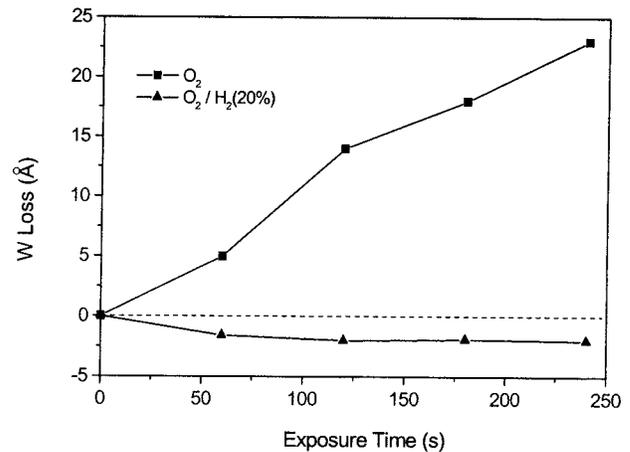


FIG. 5. Change of tungsten loss with plasma exposure time.

ously, this behavior enhances the applicability of the selective processes because the oxidation of a target can proceed as long as needed while the tungsten is kept intact.

When tungsten is oxidized by pure oxygen, the tungsten oxide can be reduced by hydrogen using post-treatment. However, compared to this approach, O₂/H₂ chemistry also demonstrates a significant advantage in reducing or controlling tungsten oxidation. As shown in Fig. 6, when tungsten is exposed to pure O₂ downstream plasma for 120 s, a tungsten film loss of 14 Å due to oxidation is generated. After the sample is then treated in a pure H₂ downstream plasma, some tungsten oxide can be reduced to tungsten so that the tungsten loss decreases. However, after about 60 s of treatment, the reducing effect disappears and the tungsten loss stays at ~7 Å up to the maximum time length of 180 s of treatment in this work. This result indicates that the H₂ post-treatment is not able to recover the tungsten loss caused by oxidation. However, in the O₂/H₂ case discussed above, tungsten loss can be easily suppressed when a small amount of H₂ is added into O₂. This difference probably can be understood for the following reason. In the case of H₂ post-treatment, hydrogen has to reduce stable WO₃ and goes be-

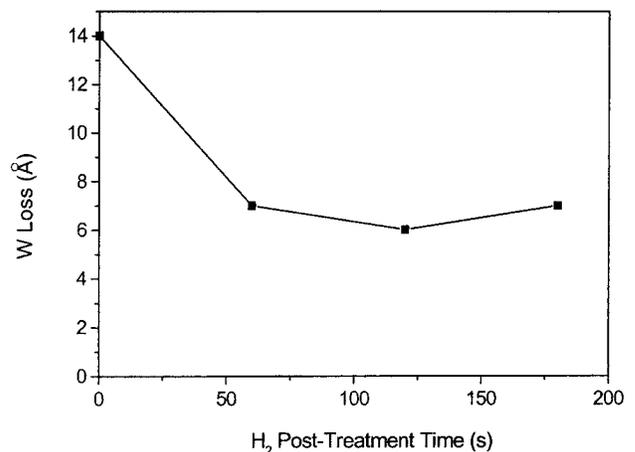


FIG. 6. Effect of H₂ post-treatment to reduce tungsten loss after oxidation in O₂ downstream plasma.

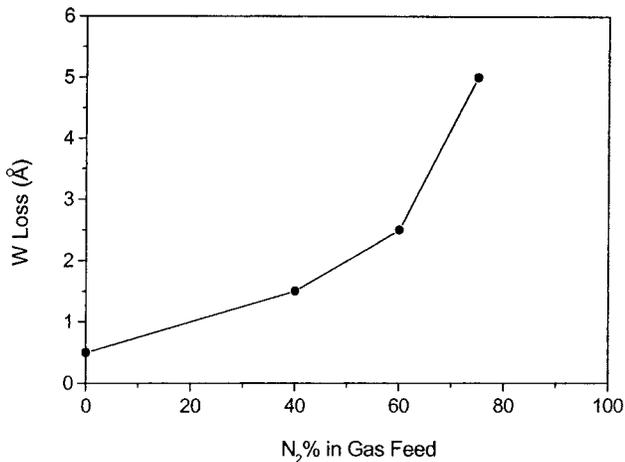


FIG. 7. Dependence of tungsten loss on N₂ addition to O₂/H₂ mixture. O₂-to-H₂ ratio=7. Plasma exposure time=120 s.

low the top surface. However, in O₂/H₂ plasma, the oxidation and reduction reactions occur simultaneously, likely on the stages of some transition states before WO₃ is formed, and are limited to the top surface.

Based on the results of O₂/H₂ chemistry, we studied the effect of N₂ addition because N₂ is a gas commonly used together with O₂ or H₂ in various plasma processing applications. We added N₂ into the O₂/H₂ plasma with a fixed O₂-to-H₂ ratio and measured the tungsten loss. As shown in Fig. 7, the O₂-to-H₂ ratio is fixed at 7 to 1 so that the tungsten loss is close to zero or almost no oxidation before N₂ addition. When N₂ is added, the tungsten loss starts to increase. As more N₂ is added, more tungsten loss or tungsten oxidation is also generated. This set of data shows that N₂ addition lowers the efficiency of H₂ in O₂ plasma for controlling tungsten oxidation, probably due to the loss of hydrogen radicals in the formation of NH_x species. As an extreme case, a so-called "forming gas" (a commercially available N₂/H₂ mixture with ~4% H₂) is mixed with O₂ and compared with O₂/H₂ chemistry for reducing tungsten oxidation. Although forming gas is commonly used as a reducing gas for plasma processing, a very small addition of O₂ (<5% in the current case) turns it into an oxidizing chemistry for tungsten, as shown in Fig. 8. Therefore, it is obvious that the O₂/forming-gas mixture cannot achieve the same performance as O₂/H₂ in controlling tungsten oxidation and meeting other process requirements simultaneously.

As the first example of the application of tungsten oxidation control, PR stripping on a tungsten gate structure is done using O₂/H₂ downstream plasma. Figure 9 gives the strip rate against the H₂% in the total gas feed. It is interesting that when H₂% is below 15%, the PR stripping is not slowed down by H₂ addition. Actually, the strip rate is slightly higher than that in the pure O₂ plasma. Since no obvious increase in oxygen radical density has been observed after H₂ addition, the small increase in PR strip rate could be due to the change in strip reaction mechanism caused by OH radicals generated in the O₂/H₂ plasma. For comparison, the result of PR stripping using the O₂/forming-gas mixture is

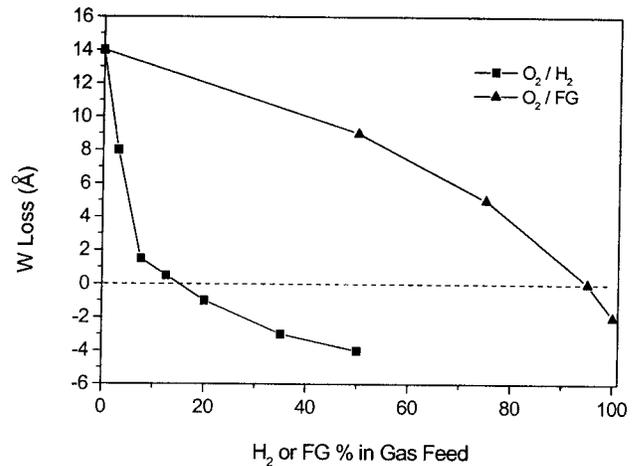


FIG. 8. Comparison of tungsten loss as a function of feed-gas composition in O₂/H₂ and O₂/forming-gas downstream plasmas. Plasma exposure time =120 s.

also plotted in Fig. 9. Based on the previous discussion, tungsten oxidation cannot be suppressed in this case unless the O₂% in the gas feed is less than 5%. Therefore, PR stripping must proceed at a much lower rate to avoid tungsten oxidation and thus significantly impacts the productivity of the application.

The second application example is selective oxidation of polysilicon over tungsten. As shown in Fig. 10, the oxidation of both silicon and tungsten occur simultaneously in O₂ downstream plasma at 300 °C. However, after H₂ is added and H₂% reaches a certain level, tungsten oxidation is suppressed. On the other hand, we found that H₂ addition can accelerate the silicon oxidation. In the example given in Fig. 10, silicon oxide growth increases significantly from around 12 Å without adding H₂ to 20 Å when 20% of H₂ is used. This result indicates that the chemical kinetics of the oxidation and reduction reactions on silicon and tungsten is quite different. While silicon seems easier to be oxidized than tungsten and/or silicon oxide seems more difficult to be reduced than tungsten oxide, the effect and mechanism of H₂

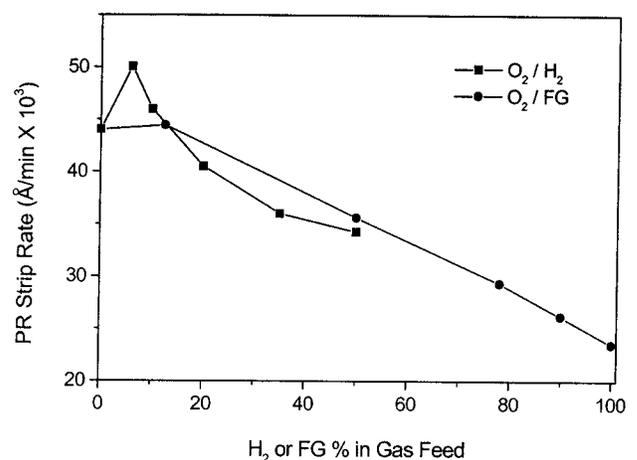


FIG. 9. PR strip rate in O₂/H₂ and O₂/forming-gas downstream plasmas.

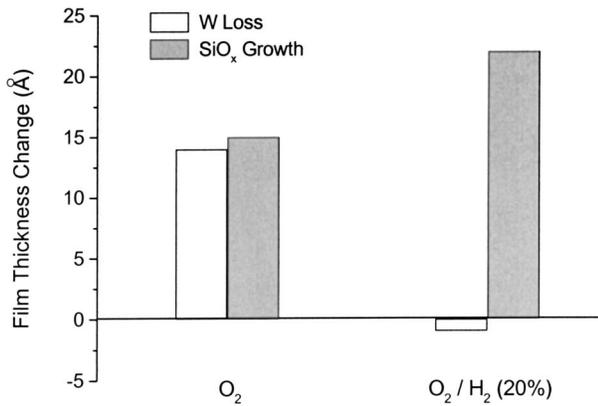


FIG. 10. Tungsten loss and silicon oxide growth in O₂ and O₂/H₂ downstream plasmas. Plasma exposure time=120 s.

addition on silicon oxidation need to be further studied. Nevertheless, the result demonstrates the possibility of selective oxidation of polysilicon over tungsten at a much lower temperature than thermal oxidation.

IV. CONCLUSION

Tungsten oxidation occurs readily in low-temperature O₂ downstream plasma by forming stable WO₃. However, the oxidation can be controlled effectively by adding H₂ into the plasma gas. The oxide growth or tungsten loss decreases rapidly with H₂% in the gas feed and becomes zero when the H₂ concentration reaches a certain low level (~15% at 300 °C). Tungsten oxidation increases significantly with sample temperature in O₂ downstream plasma. However, H₂ addition reduces the temperature dependence. This phenomenon can be explained as the result of two coexisting and competing reactions of oxidation and reduction on the surface, with the activation energy for oxidation lower than that for reduction. The tungsten oxide growth also increases linearly with plasma exposure time in pure O₂ case due to the

continuous diffusion of oxygen species through the surface oxide film toward the bulk. This behavior changes after H₂ addition. With enough H₂ in the gas mixture, tungsten oxide will not grow with time. The tungsten oxide grew in pure O₂ can also be reduced to tungsten by using H₂ post-treatment. However, the reduction is only partial even after very long treatment. The difference between H₂ addition into O₂ and H₂ post-treatment on tungsten oxidation control actually indicates that, in the former case, the competing oxidation and reduction reactions only occur at the very top surface of tungsten. When N₂ is also added into the O₂/H₂ mixture, the efficiency of H₂ in reducing tungsten oxidation is lowered, probably due to the loss of hydrogen radicals in the formation of NH_x species. Specifically, the O₂ and formation-gas mixture cannot suppress tungsten oxidation unless O₂% in the gas feed is less than 5%. Based on its effectiveness in controlling tungsten oxidation, the O₂/H₂ downstream plasma may provide good approaches for different applications where selective oxidation is required. The advantage can be seen from two examples discussed in this article, including PR stripping and polysilicon oxidation on a tungsten gate structure.

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