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Improved Diffusion Barrier Capability of Thin WSiN Film by RF Bias Application during ECR Plasma Nitridation

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1. Introduction

WSiN has been extensively used as a barrier layer in polycide gate [1], poly-metal gate [2], and Cu interconnection [3-4], because it acts as an excellent barrier against impurity or metal diffusion. We have developed an extremely thin (2～6 nm) WSiN diffusion barrier by ECR plasma nitridation. The effectiveness of the WSiN barrier can be increased by applying RF bias to the substrate during nitridation. However, the origin of this increase has not been clarified by previous explanations, such as those attributing it to the amorphous structure [3-4] or the stuffing effects of nitrogen atoms [5].

In this paper, we investigate the correlation between barrier capability and nitrogen concentration, surface composition, and the local atomic ordering of WSiN formed by ECR plasma nitridation, and explain how applying RF bias improves WSiN diffusion barrier capability.

2. Experimental Results and Discussion

2-1. *RF Bias Effect*

Thin WSiN film was formed by nitridating WSi_x surface using ECR nitrogen plasma with or without RF bias. $WSi_{2.6}$ was deposited by sputtering at 320°C. WSiN film thickness varies depending on the nitridation condition. The impurity distribution is different for various WSiN film thicknesses even though the films have the same diffusion barrier capability. Therefore, to evaluate barrier capability independently of film thickness, we converted phosphorus (P) distribution to the diffusion coefficient for P in WSiN (D_P). Figure 1 shows the dependence of D_P on the nitridation condition. D_P with RF bias is over one order of magnitude smaller than that without RF bias. That is, the WSiN barrier capability is improved by RF bias application.

2-2. *Nitrogen Concentration*

The relationship between D_P and nitrogen concentration in WSiN is shown in Fig. 2. WSiN films with RF bias has a higher nitrogen concentration than that without RF bias. Comparing WSiN films with RF bias, D_P decreases as nitridation time increases, even though nitrogen concentration is almost the same. This result indicates the barrier capability does not depend on only nitrogen concentration.

2-3. *Surface Composition*

Figure 3 shows XPS spectra of WSiN. Si-rich WSiN was formed without RF bias. On the other hand, the Si $2p$ peak almost disappeared by applying RF bias. RF bias makes the energy of nitrogen ions increase. XPS data suggest the bombardment effect of nitrogen ions is remarkably enhanced by RF bias and Si atoms are preferentially sputtered.

2-4. *Local atomic ordering of WSiN*

The degree of atomic ordering in amorphous WSiN can be lowered by reducing WSi_x deposition temperature, because more disordered WSi_x is nitridated. The relationship between D_P and deposition temperature of WSi_x is shown in Fig. 4. D_P becomes smaller as the deposition temperature decreases. That is, the WSiN barrier capability increases as the degree of atomic ordering in amorphous WSiN film is lowered. Many amorphous films keep their local atomic ordering, as observed in WSiN formed by reactive sputtering [5]. To compare the degree of local atomic ordering, the radial distribution around nitrogen atoms was analyzed by N-K edge EXAFS for WSiN, as shown in Fig. 5. A definite peak at 1.4 Å was observed without RF bias, while no obvious peak was observed with RF bias. The disappearance of the peak means that the local atomic ordering in amorphous structure is lowered by RF bias. These results in Figs. 4 and 5 confirm that barrier capability also depends on the local atomic ordering of WSiN.

2-5. *Diffusion Barrier Mechanism*

Without RF bias, nitrogen atoms enter interstitial sites of WSi_x without disordering its atomic structure. On the other hand, nitrogen ions accelerated by RF bias strike the WSi_x surface. As a result, the nitrogen concentration increases, Si is preferentially sputtered and the local atomic ordering of WSiN is lowered. Figure 6 is a schematic diagram of the diffusion barrier mechanism of WSiN. With RF bias, diffusion paths such as interstitial sites are plugged up by nitrogen atoms that locate in the disordered interstitial sites. Therefore, WSiN film formed by applying RF bias effectively suppresses phosphorus diffusion.

3. Conclusion

Thin WSiN film shows excellent barrier capability when RF bias is applied to the substrate during ECR plasma nitridation. RF bias makes the energy of nitrogen ions increase, and accelerates the nitrogen ions striking the WSi_x surface. As a result, the nitrogen concentration increases and Si is preferentially sputtered. Furthermore, the local atomic ordering in thin WSiN film is lowered. We found that these factors contribute to the suppression of phosphorus diffusion through interstitial sites.

Acknowledgments

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References

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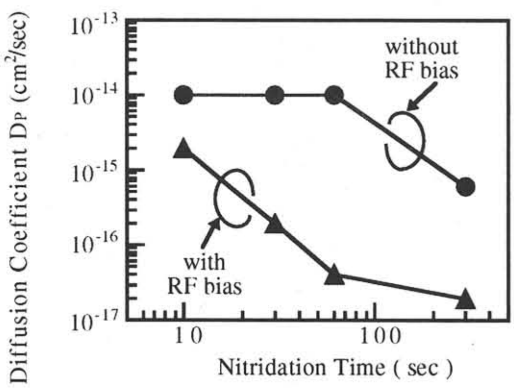

Fig. 1 Diffusion coefficient for P in WSiN (D_P) as a function of the nitridation condition. D_P was determined by comparing the impurity distribution after annealing (850 °C, 60 min) with the T-SUPREM simulation result. D_P above 1×10^{-14} cm²/sec is indefinite because P diffusion is very fast and unobservable.

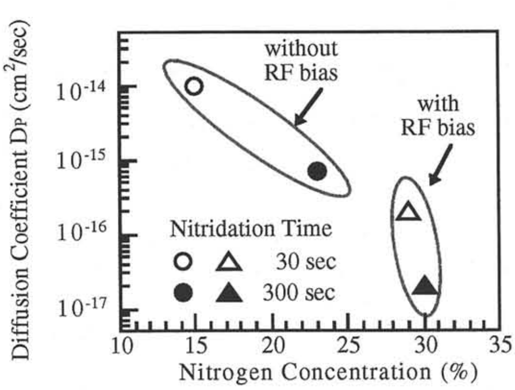

Fig. 2 Relationship between the nitrogen concentration in WSiN and the diffusion coefficient for P in WSiN (D_P). D_P above 1×10^{-14} cm²/sec is indefinite for the same reason as in Fig. 1.

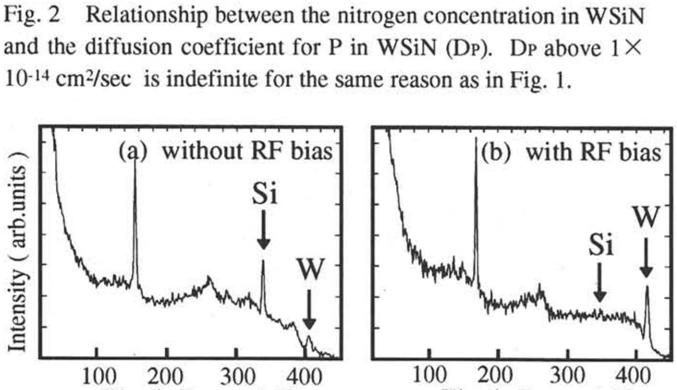

Fig. 3 XPS spectra of WSiN (a) without RF bias and (b) with RF bias. (h ν = 450 eV)

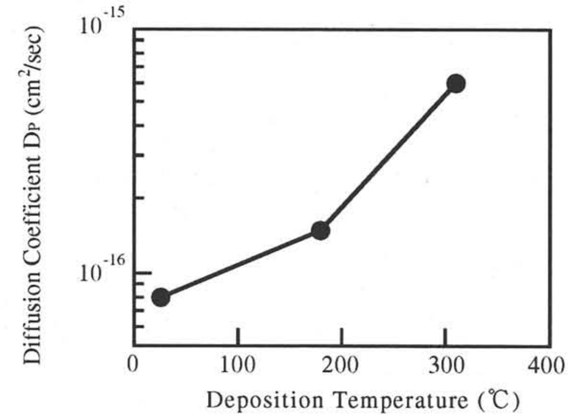

Fig. 4 Diffusion coefficient for P in WSiN (D_P) as a function of WSi_x deposition temperature. Nitridation time is 300 sec without RF bias. The annealing condition is 850 °C for 60 min.

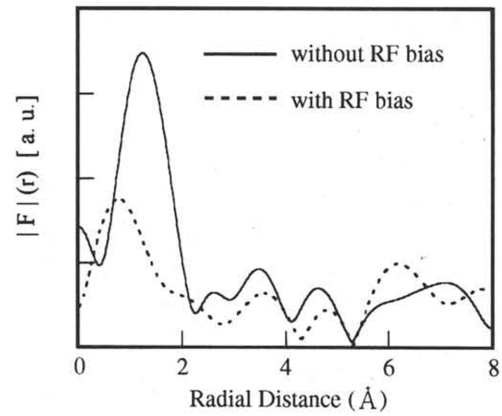

Fig. 5 Radial distribution around nitrogen atoms for WSiN, which was obtained by the Fourier transform of N-K edge EXAFS. The horizontal axis is the distance from a nitrogen atom and the longitudinal axis is the Fourier transform magnitude. The nitridation time is 300 sec with or without RF bias.

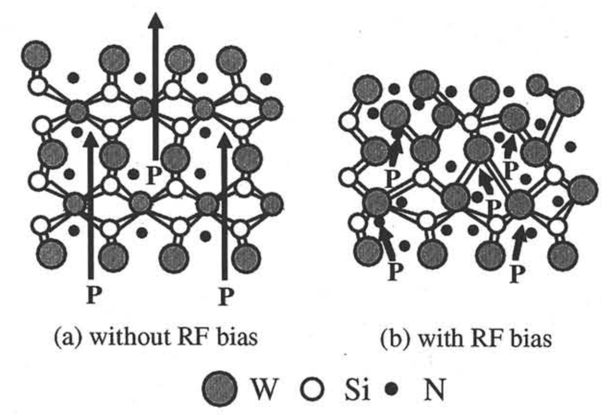

Fig. 6 Schematic diagram showing the diffusion barrier mechanism of WSiN (a) without RF bias and (b) with RF bias.