Extended Abstracts of the 1998 International Conference on Solid State Devices and Materials, Hiroshima, 1998, pp. 26-27

New PentaCoordinated Si(PCS) Model for SiN CVD Mechanism

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1. Introduction

Recently, the reduction trend of gate oxide thickness is accelerated to improve the performance of MOSFETs. In the ultra thin region, the high leakage current due to the direct tunneling through the oxide is one of the most serious issue to be solved.

For future devices, SiN film is the promising candidate to achieve thin gate dielectric because of its higher dielectric constant. However, the actual SiN film includes many defects, which result in the high leakage current.

To reduce the leakage current, we proposed the novel TCS-SiN film using $SiCl_4$ and NH_3 as source gases for DRAM capacitor application[1]. The leakage current of TCS-SiN is lower than that of the conventional DCS-SiN using $SiCl_2H_2$ and NH_3. To understand the leakage current difference, the deposition mechanism of TCS- and DCS-SiN has to be clarified. The SiN deposition model was already reported by S. Koseki et. al.[2]. A comprehensive understanding of the reaction without decomposition of the source gases is still lacking.

In this paper, the new PCS(PentaCoordinated Si) model for SiN CVD mechanism, is proposed from the calculation results of the MO(Molecular Orbital) method. From the deposition mechanism difference, superior film properties of TCS-SiN were confirmed.

2. PCS model for TCS-SiN deposition mechanism

The MOPAC program using semi-empirical MO method was applied for all calculations.

PCS reaction is consisted of two steps and the first step is NH_3 addition and the next one is HCl elimination. The first step of the reaction between TCS and NH_3 is shown in Fig.1. As the distance between Si of TCS and N of NH_3 decreases, the enthalpy of TCS-NH_3 system decreases. The enthalpy of TCS-NH_3 system becomes a minimum at the distance of about 0.22nm and Fig.2 shows its optimized structure, which contains the pentacoordinated Si(PCS). This means that the Si atom of TCS lacks the electron because of the large electronegativity of Cl and PCS becomes stable by the lone pair of NH_3. The reaction of the NH_3 addition has no energy barrier and the heat of this reaction is -53kJ/mol. On the next HCl elimination step, the transition state was determined as shown in Fig.3 and the activation energy from $SiCl_4(NH_3)$ is about 54kJ/mol. These results are summarized as the energy diagram in Fig.4. The total activation energy of PCS reaction is very small because of the energy gain at the NH_3 addition step unless $SiCl_4(NH_3)$ lose the energy gain by inelastic collision.

On the basis of the PCS reaction, SiN deposition mechanism is explained, as follows. In the vapor phase, the precursors of $SiCl_2(NH_2)_2$, $(SiCl_3)_2NH$ and so on, are produced. Simultaneously on the SiN film surface, the Cl bonded Si of TCS and the precursors reacts with the lone pair of the surface N atoms and the lone pair of NH_3 and the precursors reacts with the Cl bonded surface Si atoms.

3. Model for DCS-SiN deposition mechanism

The PCS reaction on DCS is almost same as that on TCS, as shown in Reaction 1 to 6 of Table I. DCS has two hydrogen atoms. It is calculated in Ref.2 that the hydrogen eliminates from DCS and the activation energy is about 168kJ/mol. Its value is much larger than that of PCS reaction, as shown in Reaction 3 and 7. From these results, it is expected that many Si-H bonds remain in DCS-SiN.

4. Relations between model and actual characteristics

FT-IR spectra of SiN film are shown in Fig.5. There is no Si-H bond in the TCS-SiN and many Si-H bonds in DCS-SiN, and this result supports the proposed PCS model. Since the bond strength of Si-H is weak, Si-H bond easily forms Si dangling bond. It was reported that Si dangling bond is the electron and hole trap site[3]. Fig.6 shows the ESR spectra of TCS- and DCS-SiN. Since the dangling bonds in TCS-SiN are reduced compared with DCS-SiN, the leakage current of TCS-SiN is about one order lower than that of DCS-SiN, as shown in Fig.7.

5. Conclusion

We proposed the PCS model as SiN CVD mechanism. From the deposition mechanism, we clarified the reason why DCS-SiN is incorporated in more Si-H bonds than TCS-SiN and confirmed the TCS-SiN superiority.

Acknowledgment

Aurthors wish to thank Yasushi Nakasaki for many important suggestions of calculation results.

References

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[2]S. Koseki and A. Ishitani: J. Appl. Phys. **72** (1992) 5808

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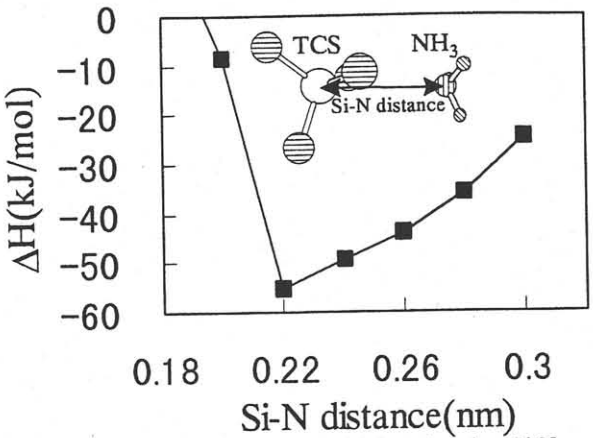

Fig. 1 Enthalpy of $SiCl_4$-NH_3 system is plotted against Si-N distance.

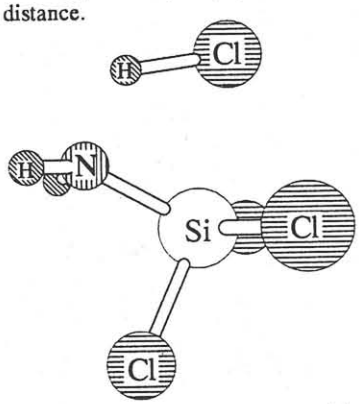

Fig. 3 Geometrical structure of the transition state at the HCl elimination

Table I. Energetics for elementary reaction of SiN deposition
Ea is a activation Energy and ΔH is a heat of reaction (kJ/mol)

reactants	products	Ea	ΔH
1. $SiCl_2H_2$+NH_3	$SiCl_2H_2(NH_3)$	0	-51
2. $SiCl_2H_2(NH_3)$	$SiClH_2(NH_2)$+HCl	+55	+54
3. $SiCl_2H_2$+NH_3	$SiClH_2(NH_2)$+HCl	+4	+3
4. $SiCl_4$+NH_3	$SiCl_4(NH_3)$	0	-53
5. $SiCl_4(NH_3)$	$SiCl_3(NH_2)$+HCl	+54	+48
6. $SiCl_4$+NH_3	$SiCl_3(NH_2)$+HCl	+1	-5
7. $SiCl_2H_2$	$SiCl_2$+H_2	+168	+168[a]

[a] Calculation value taken from Ref. 2

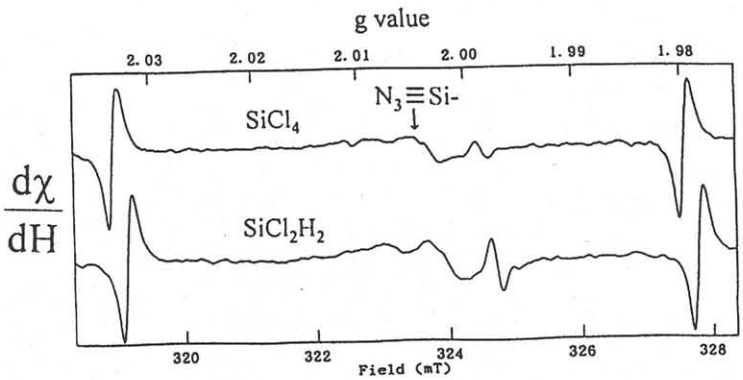

Fig. 6 ESR Spectra of TCS-SiN and DCS-SiN

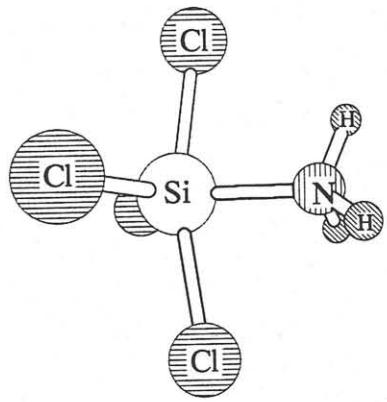

Fig. 2 Geometrical structure of minimum at the NH_3 addition

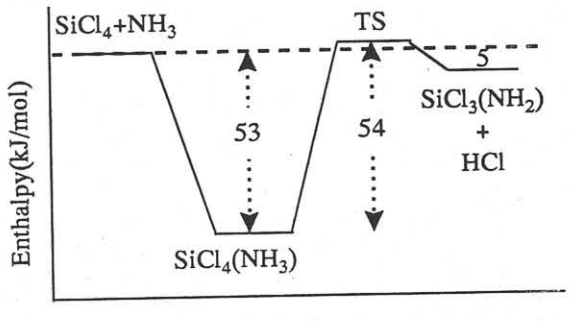

Fig. 4 Energy diagram of $SiCl_4$-NH_3 system

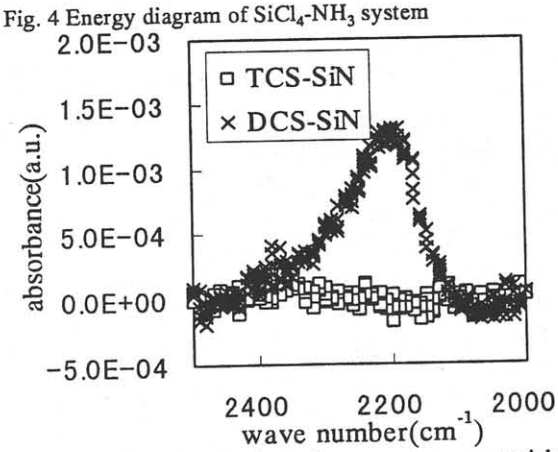

Fig. 5 Si-H bond density dependency on source material by FT-IR measurement

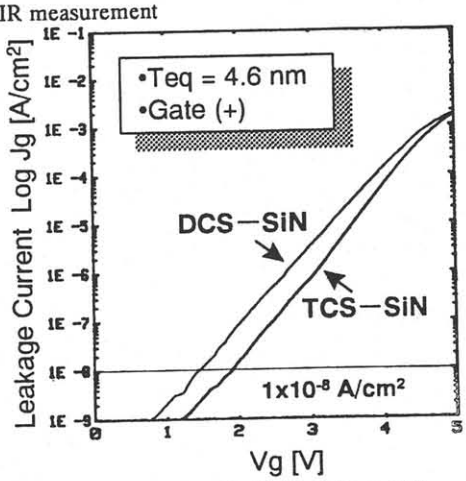

Fig. 7 J-V characteristics of TCS-SiN and DCS-SiN