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Low-Temperature Chemical-Vapor-Deposition of Silicon-Nitride Film from Hexachloro-Disilane and Hydrazine

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We have successfully deposited SiN films at temperatures as low as 350℃ by CVD method using hexachloro-disilane (Si_2Cl_6) and hydrazine (N_2H_4). Atomic ratio (N/Si) of the film deposited at 400℃ was 1.3. Total hydrogen content was about 25atomic%. The breakdown-field strength was 5.3MV/cm at leakage-current density of 1 μ A/cm^2, and the low-field resistivity was more than 10^{15} Ω cm. Amorphous-silicon thin-film transistors equipped with this film as the gate dielectric showed good transfer characteristics.

1. INTRODUCTION

Much attention has been paid recently to low-temperature (less than 400℃) deposition method of silicon nitride (SiN), since the SiN film deposited at low temperatures is important as a passivation layer for ULSI chips and a gate insulator for thin film transistors TFTs. Plasma-enhanced CVD (PECVD) is the representative method for low temperature deposition of the SiN film. However, there are fatal drawbacks in the PECVD arising from inherent properties of plasma. Low temperature CVD, i.e., alternative method is also attractive but its lowest deposition temperature is still as high as 400℃ even by use of trisilane (Si_3H_8) and hydrogen azide (HN_3)[1]. Application of higher silanes and nitrogen hydrides to reduce the deposition temperature encounters the serious limitation that they are thermally unstable even under room temperature.

We have proposed CVD method which can utilize advantage of electrostatic energy in the source molecule. It has been reported that the CVD temperature is lowered to about 600℃ by using $SiCl_4$ and NH_3[2] due to strong dipole moments existing between Si-Cl and N-H bonds. Since higher, but still thermally stable, source molecules are expected to react more easily with each other, we investigated CVD using Si_2Cl_6 and N_2H_4.

2. DEPOSITION CHARASTERISTICS

Figure 1 is a schematic of the apparatus used in this study. Since both Si_2Cl_6 and N_2H_4 are liquid at room temperature, they were introduced into the chamber by using N_2 carrier gas. The standard deposition conditions are given in Table 1.

Deposition rate **DR** and refractive index **n** are shown in Fig.2 as a function of reciprocal substrate temperature T. They were 6000 Å/h and 1.75 at T=450℃, respectively, and decreased with T gradually for T > 350℃

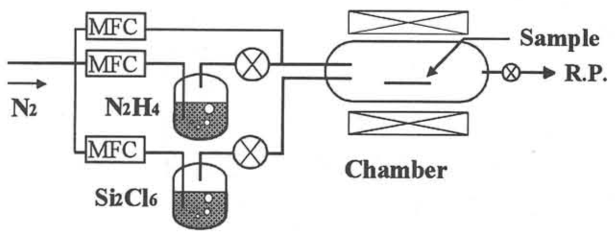


Figure 1. Schematic view of CVD system

Table 1. Standard deposition conditions

Pressure in Bubbler	760Torr
Total N_2 Gas Flow	100sccm
Chamber Pressure	160Torr
Substrate Temperature	400℃
N_2H_4 Carrier Gas Flow Rate	80sccm[0.98sccm]
Si_2Cl_6 Carrier Gas Flow Rate	20sccm[0.12sccm]

*[ ]: Net Gas Flow Rate

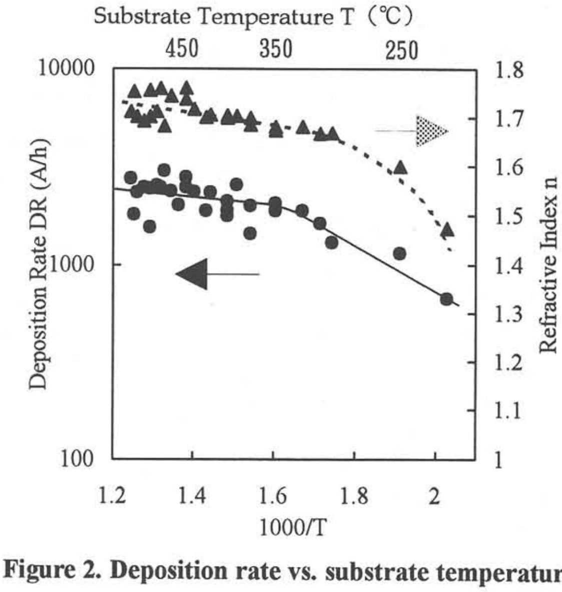
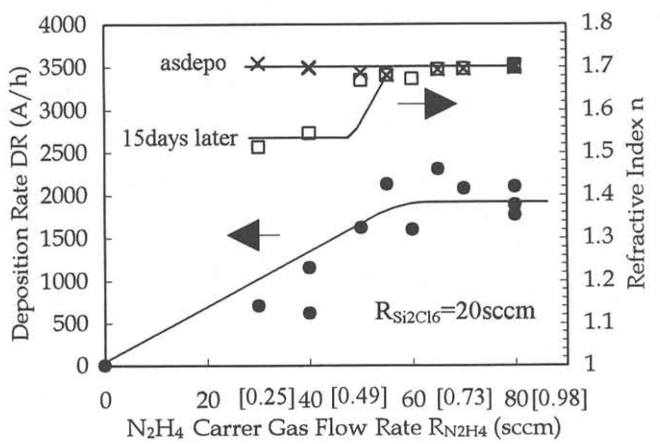


Figure 2. Deposition rate vs. substrate temperature

but rapidly for T < 350℃. This result might be caused by residual NH_4Cl by-product which has the sublimation temperature of 338℃.

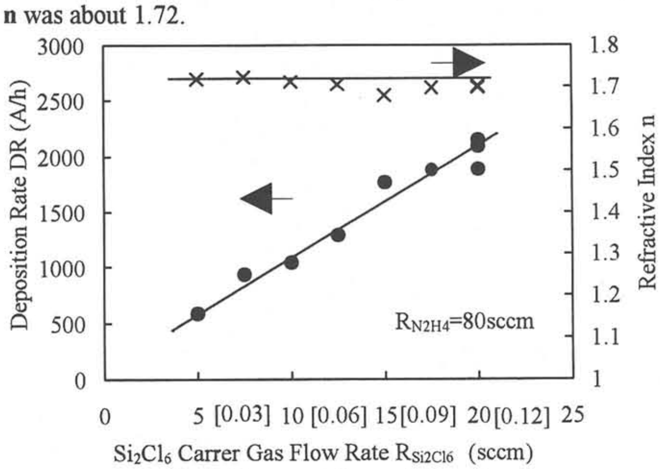
DR and **n** are shown in Fig.3 as a function of N_2H_4 carrier gas flow rate $\mathbf{R}_{N2H4}$ where the Si_2Cl_6 carrier gas flow rate $\mathbf{R}_{Si2Cl6}$ was kept at 20sccm. **DR** was increased with $\mathbf{R}_{N2H4}$ for $\mathbf{R}_{N2H4}$ < 60 sccm, but was saturated for $\mathbf{R}_{N2H4}$ > 60 sccm, since deposition kinetics became transport-limited by Si_2Cl_6 molecules. **n** was about 1.7 for all conditions, but it was decreased gradually for the sample formed by $\mathbf{R}_{N2H4}$ < 60 sccm with elongating storage time in atmosphere and finally saturated at 1.46. Results of Auger electron spectroscopy (AES) and Fourier transform infrared spectrometer (FTIR) measurements indicated that these films were Si rich at first, and that Si-N bonds was substituted gradually by Si-O bonds to form stoichiometric SiO_2.



[ ]: N_2H_4 gas net flow rate (sccm)

Figure 3. Deposition rate and refractive index vs. N_2H_4 flow rate

DR and **n** are shown in Fig.4 as a function of $\mathbf{R}_{Si2Cl6}$ where $\mathbf{R}_{N2H4}$ was kept at 80sccm. Since the deposition kinetics were transport-limited by Si_2Cl_6 molecules, the deposition rate was a linear function of $\mathbf{R}_{Si2Cl6}$. In these conditions, **n** was about 1.72.



[ ]: Si_2Cl_6 gas net flow rate (sccm)

Figure 4. Deposition rate and refractive index vs. Si_2Cl_6 flow rate

3. STRUCTURAL PROPERTIES

Figure 5 shows FTIR absorption spectrum for the film deposited under standard conditions. Strong absorption peaks were near 870cm^{-1} for Si-N stretching modes and 460cm^{-1} for its breathing modes, indicating that the main component of the film was Si-N bonds. There were additional peaks around 3350cm^{-1} and 1185cm^{-1} for N-H stretching and bending modes, respectively. The hydrogen content estimated from the peak around 3350cm^{-1} was 25 atomic%[3]. Si-H bonds was not detected.

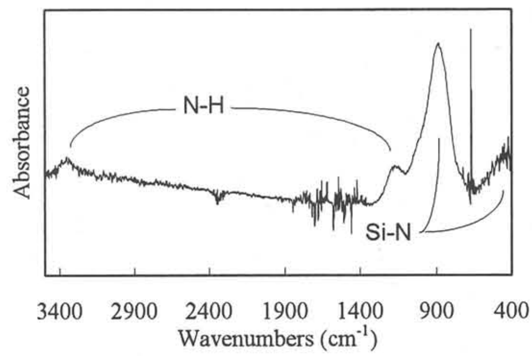


Figure5. FTIR absorbance spectrum

Figure 6 shows Si 2p X-ray photoelectron spectroscopy (XPS) spectrum for the film deposited under standard deposition conditions and the result of decomposition. Si 2p spectrum can be interpreted into five tetrahedrons such as $Si_{5-n}N_n$(n=0~4) bonding configurations.[4] Since there were no Si-H bonds, only Si-N bonds should be considered. As shown in the figure, the stoichiometric Si-N_4 structure dominated the components, and there were only small quantities of Si_2N_3, Si_3N_2 and Si_4N components but not Si-Si_4 component.

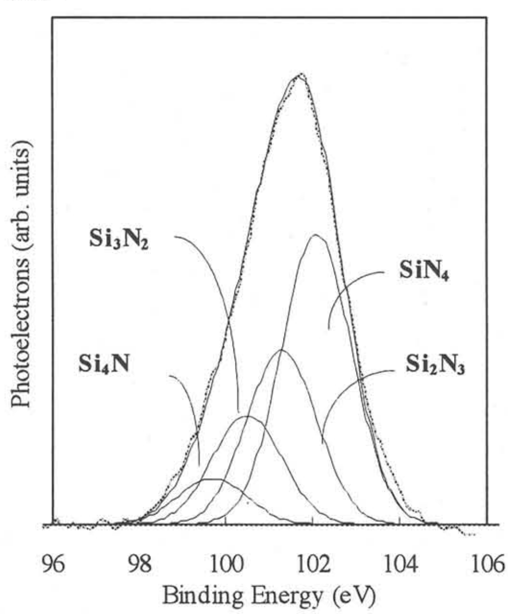


Figure 6. Si 2p spectrum of SiN film and a result of decomposition

4. ELECTRICAL PROPERTIES

Figure 7 shows logarithmic current density J as a function of square root of field strength E across the film deposited under the standard conditions. The optical dielectric constant calculated from J-$E^{1/2}$ slope in the high field region was 3.0, which is equal to square of the refractive index **n** (**n**=1.72). This result led us to the conclusion that the conduction mechanism in the high field region was dominated by Frenkel-poole emission.[5] The breakdown-field strength determined from the field-strength at 1 μA/cm^2 was 5.3MV/cm. The static dielectric constant calculated from the capacitance under accumulation condition was about 5.6 for all films.

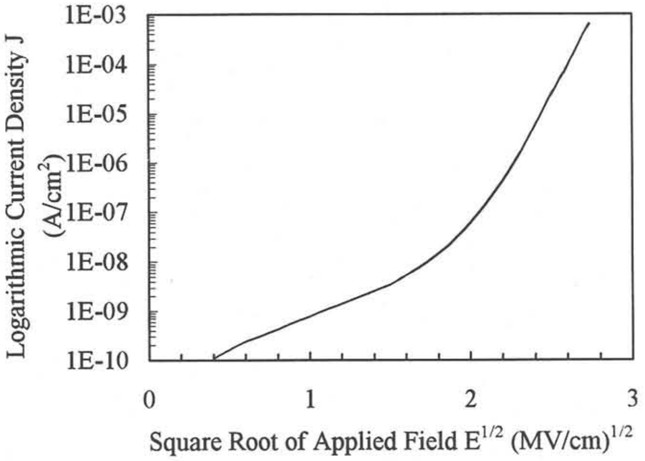


Figure 7. J-E characteristics of SiN film

5. a-Si TFT CHARACTERISTICS

The a-Si/SiN TFT fabricated in this study was of a simple inverted staggered gate structure with highly doped single-crystal silicon as the gate electrode, as shown in Fig.8 . The 200nm-thick SiN layer was deposited under the standard deposition conditions. The a-Si layer of 35 nm-thick was deposited by PECVD method at 300 ℃. Al was evaporated directly onto the a-Si film for formation of electrodes.

Logarithmic drain current I_d is shown in Fig.9 as a function of gate voltage V_g for drain voltage V_d of 5V. The threshold voltage and the mobility were 26V and 0.64cm^2/Vs, respectively. The high threshold voltage will be caused by breaking vacuum between depositions of the SiN and a-Si films. The on/off current ratio was greater than 10^5 for all samples.

6. CONCLUSIONS

The SiN film has been deposited at temperatures as low as 350℃ using Si_2Cl_6 and N_2H_4 gas mixture. The breakdown-field strength and the low-field resistivity of the film deposited at 400℃ were 5.3MV/cm and more than 10^{15} Ω cm, respectively. The a-Si TFT with this SiN film as gate dielectric showed good device characteristics. The field-effect mobility and threshold voltage were 0.55cm^2/Vs and 26V, respectively. Film properties appeared that this CVD gas combination is interesting as the TFT gate insulator.

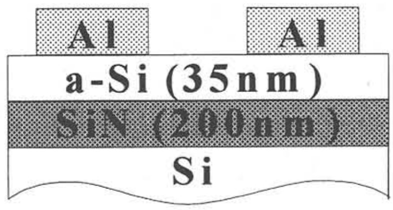


Figure 8. Cross sectional view of a-Si TFT

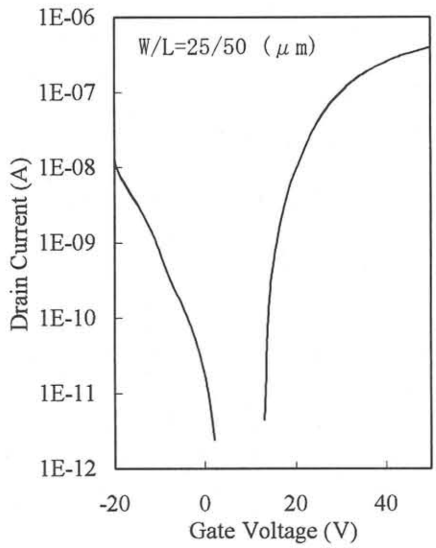


Figure 9. I_d-V_g characteristics of a-Si/SiN TFT

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