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Optical and Electrical Properties of Amorphous Silicon Nitride Films Prepared at High Deposition Rate

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We deposited a-SiN_x:H ($x \simeq 1.2$) films at high deposition rates using the substrate impedance tuning method in glow-discharge decomposition. Optical absorption spectra in the near ultraviolet region shifted toward the higher energy side as the films were deposited at the higher rate. In electrical properties, leakage current decreased and dielectric field strength increased with an increase of deposition rate.

§1. Introduction

Amorphous silicon nitride is an important material for surface passivation layer of LSI because of the excellent barrier effect for alkali-ion and the good electrical insulation of the material. The film of hydrogenated amorphous silicon nitride (a-SiN_x:H) is prepared by the plasma-enhanced-chemical-vapor-deposition method at low temperatures (250~350 °C), which is one of necessary process conditions in LSI technology.

Another important demand is to fabricate a-SiN_x:H film at high deposition rate in order to improve the throughput of the process. We fabricated a-SiN_x:H films at a high deposition rate (2.2 nm/s) using the substrate impedance tuning method[1] in glow-discharge decomposition.[2] As the deposition rate of the film in this method increased, the atomic density increased and BHF etch rate decreased.[2]

In this paper, we report the optical absorption edge and electrical properties of the high rate deposition films. We compared the electrical properties of the high rate deposition films with those of the low rate deposition films in this work and the films in references 3) and 4).

§2. Experimental

As shown in Fig. 1, an apparatus for the substrate impedance tuning method is equipped with a mesh surrounding two parallel electrode disks and with an external inductance, which connects substrate electrode and the ground. Effective glow-discharge decomposition of SiH_4 and NH_3 gases was carried out in the space surrounded by the electrodes and the mesh. Flow rates of pure SiH_4 and pure NH_3 were 30 and 228 sccm, respectively. Total pressure was 0.25 Torr, rf power 90W and substrate temperature 250 °C. Films deposited at various deposition rates were obtained at the same flow rate, rf power, total pressure and substrate temperature by varying substrate impedance. The highest deposition rate (≃2.2 nm/s) was achieved

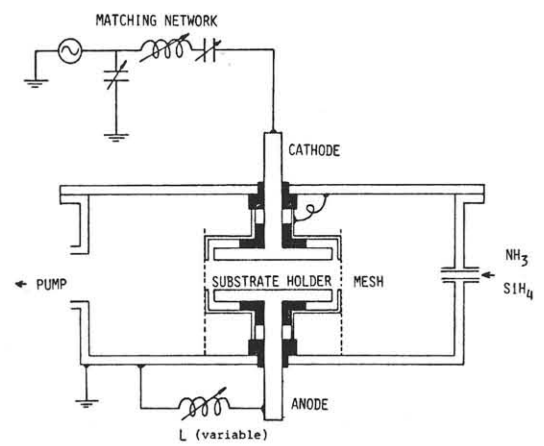

Fig. 1 Experimental system for plasma-enhanced chemical vapor deposition with substrate tuning network.

when the resonance condition in the circuit composed of the inductance between the substrate and the ground and the substrate sheath capacitance was satisfied. The lowest deposition rate ($\approx$0.23 nm/s) was obtained at the condition that no external inductance was connected.

The absorption coefficient of films were determined by measurement of transmittance of films in the thickness range 0.7 to 1.5 μm on quartz. The film thickness was estimated from the interference of transmittance in the near infrared region.

Electrical measurements were carried out in a dry-N_2 box for the films in the range 70 to 100 nm on n^+-Si (100). The film thickness in that range was measured with an ellipsometer using a mercury arc source (546.1nm).

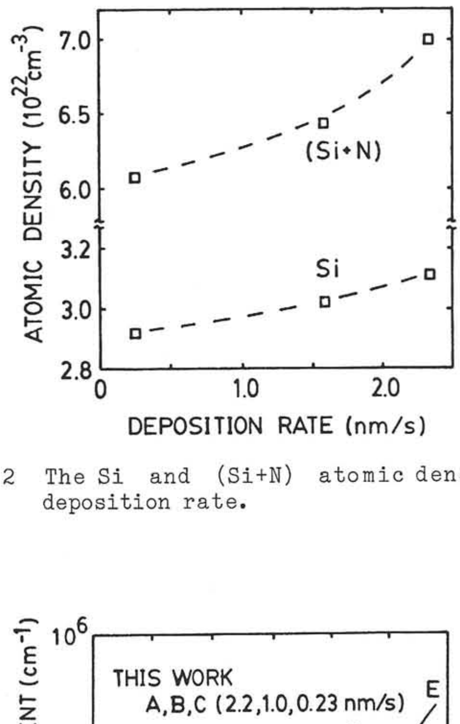

Fig. 2 The Si and (Si+N) atomic density for deposition rate.

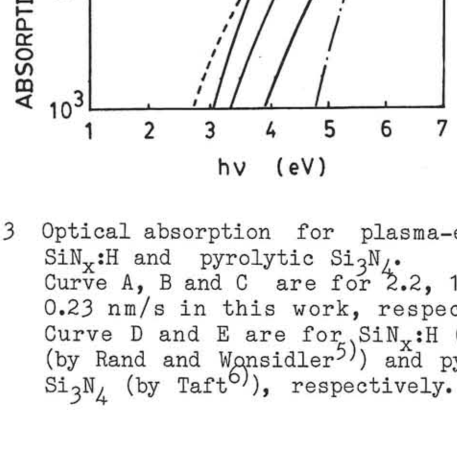

Fig. 3 Optical absorption for plasma-enhanced SiN_x:H and pyrolytic Si_3N_4. Curve A, B and C are for 2.2, 1.0 and 0.23 nm/s in this work, respectively. Curve D and E are for SiN_x:H (x=1.22) (by Rand and Wonsidler[5]) and pyrolytic Si_3N_4 (by Taft[6]), respectively.

§3. Results and Discussion

3.1 Elemental composition and chemical states

Films prepared by glow-discharge decomposition of pure SiH_4 and pure NH_3 gases were composed of the elements of Si, N and H. The atomic ratio N/Si estimated by means of XPS measurements was in the range of 1.0 to 1.2 and nearly constant. On the other hand, the bond concentration ratio (N-H)/(Si-H) considerably increased with an increase of deposition rate. The hydrogen concentration estimated from absorption coefficient in infrared region was in the range of 20 at%. As the deposition rate of the film increased, the hydrogen concentration decreased and the valence electron density increased. This result indicates an increase of Si and N atomic density. Figure 2 shows that Si and (Si+N) atomic density increase with an increase of deposition rate.

3.2 Optical properties

Absorption curves for plasma-enhanced SiN_x:H films (A, B, C and D) and pyrolytic Si_3N_4 (E) are shown in Fig. 3. Curve A, B and C are absorption spectra for our samples, whose deposition rates

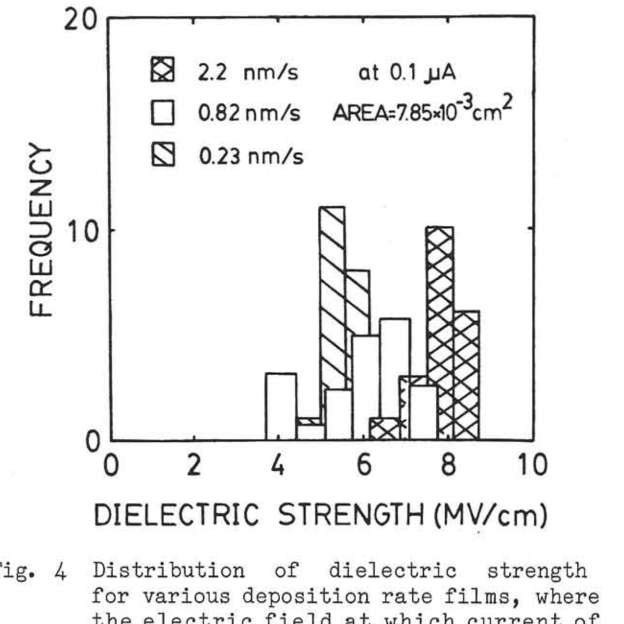

Fig. 4 Distribution of dielectric strength for various deposition rate films, where the electric field at which current of 10^{-7} flows is used as dielectric strength.

are 2.2, 1.0 and 0.23 nm/s, respectively. Curve D is for a plasma-enhanced SiN_x:H (x=1.22) reported by Rand and Wonsidler[5]. Curve E is for pyrolytic Si_3N_4 reported by Taft[6]. Curve C for the low deposition rate (0.23 nm/s) film shows the spectrum similar to curve D. As deposition rate of the film in the present work increases, absorption spectrum approaches to curve E.

Rand and Wonsidler had found a good correlation between absorption edge energy and film composition (Si/N). Our high deposition rate film is very different from their film in optical absorption. We considered this difference as a difference in the structure related with Si-H and N-H bonds. As the bond concentration ratio (N-H)/(Si-H) increases, absorption curve shifts toward the higher energy side.

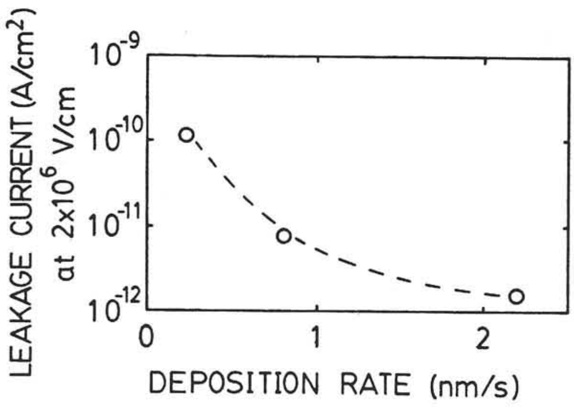

Fig. 6 Leakage current at 2×10^6 V/cm for deposition rate.

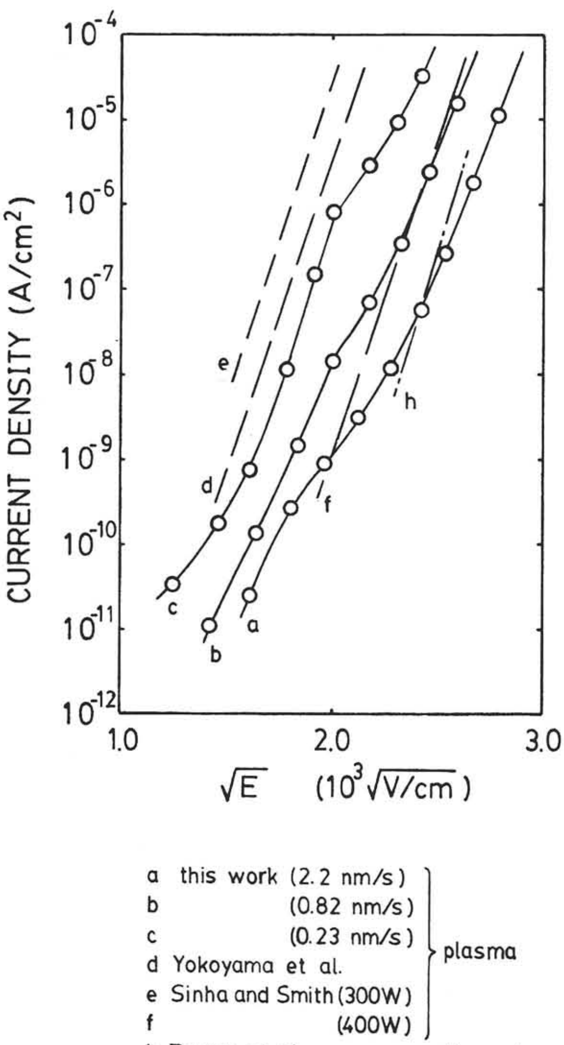

Fig. 5 Current-voltage characteristics of plasma SiN_x:H (a, b, c, d, e and f) and pyrolytic Si_3N_4 (h).

3.3 Electrical properties

Frequency distribution of dielectric strength is indicated in Fig. 4, where dielectric strength is defined as the field at which current of 10^{-7} A flows. This figure shows that maxima of the distribution are at about 7.8, 6.7 and 5.3 MV/cm for films deposited at 2.3, 0.82 and 0.23 nm/s, respectively. Dielectric strength increases as the film is deposited at the higher rate.

Figure 5 shows current-voltage (I-V) characteristics of plasma SiN_x:H and pyrolytic Si_3N_4 with Poole-Frenkel plot. Curve a, b and c represent results for our films deposited at 2.2, 0.82 and 0.23 nm/s, respectively. The I-V characteristics (curve c) of low deposition rate (0.23 nm/s) film is similar to curve d (by Yokoyama et al.[3]) and e (by Sinha and Smith (300 W)[4]). As deposition rate of the film increases from c to a, I-V curve shifts toward the side of lower leakage current. Leakage current at a low field of 2×10^6 V/cm is shown versus deposition rate in Fig. 6. Curve c, d and e are I-V curves of conventional plasma-enhanced SiN_x:H films. Curve b (middle deposition rate film) is similar to curve f (by Sinha and Smith (400 W)[4]) in the higher field range. Curve a (high deposition rate film) represents I-V charateristics of low leakage current like curve h of pyrolytic Si_3N_4 (by Brown et al.[7]).

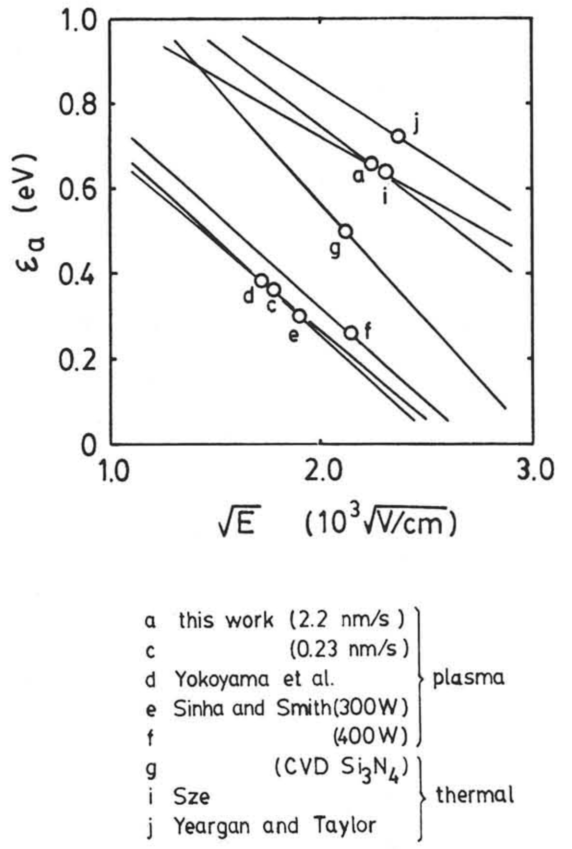

Fig. 7 Relation between activation energy and applied field. Circles are measured-points.

A slope of Arrhenius plot of leakage current at the field dominated by a Poole-Frenkel emission indicate activation energy (ε_a) for Poole-Frenkel emission. Figure 7 shows the relations between an applied field and the activation energy. In this figure, the circles are measured points and the lines are calculated using dynamic dielectric constant estimated from slope of Poole-Frenkel plot of I-V characteristics. Energy extrapolated to zero applied field show the barrier hight for Poole-Frenkel emission. As the barrier hight is larger, Poole-Frenkel emission current will be less. In fig. 7, a, c, d, e and f are for plasma-enhanced SiN_x:H and g, i and j are for pyrolytic Si_3N_4. Curves c, d, e and f for plasma SiN_x:H films are almost superposed. On the other hand, the curve of high deposition rate film (a) is located nearly at those of pyrolytic Si_3N_4 (g, i and j). This result may relate with the structure and optical properties of this film.

§ 4. Conclusion

High deposition rate SiN_x:H films can be prepared by glow-discharge decomposition of SiH_4 and NH_3 using the substrate impedance tuning method. The high deposition rate films have following properties: in the structure, the atomic ratio N/Si is nearly constant ($\approx$1.1), the bond concentration ratio (N-H)/(Si-H) is larger than 1 and the atomic density increases by the high deposited condition. In the optical properties, the absorption edge is in higher energy side as for pyrolytic Si_3N_4. In the electrical properties, leakage current is less and dielectric strength is larger, as compared with that of conventional SiN_x:H films.

References

1) T. Hamasaki, M. Ueda, A. Chayahara, M. Hirose and Y. Osaka, Appl. Phys. Lett. 44 (1984) 1049.

2) Y. Nishibayashi, T. Imura, Y. Osaka, K. Shizuma and F. Nishiyama, Jpn. J. Appl. Phys. 24 (1985) 469.

3) S. Yokoyama, N. Kajihara, M. Hirose, Y. Osaka, T. Yoshihara and H. Abe, J. Appl. Phys. 51 (1980) 5470.

4) A. K. Sinha and T. E. Smith, J. Appl. Phys. 49 (1978) 2756.

5) M. J. Rand and D. R. Wonsidler, J. Electrochem. Soc. 125 (1978) 99.

6) E. A. Taft, J. Electrochem. Soc. 118 (1971) 1341.

7) G. A. Brown, W. C. Robinette, Jr. and H. G. Carlson, J. Electrochem. Soc. 115 (1968) 948.

8) S. M. Sze, J. Appl. Phys. 38 (1967) 2951.

9) J. R. Yeargan and H. L. Taylor, 115 (1968) 273.