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High Rate Selective Etching of a-Si:H and Modification Effect of a-SiN$_x$:H Surface by Hydrogen Radical

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High rate selective etching of a-Si:H was achieved by using a hydrogen microwave afterglow technique. This indicates the strong etching effect of hydrogen radicals. To clarify the effect of modifying an a-SiNx:H surface by hydrogen radicals, ultrathin a-SiNx:H layers were stacked intermittently on a substrate by a NH_3 microwave afterglow method, hydrogen-radical treatment was carried out between each layer deposition cycle. The atomic composition (N/Si) and hydrogen-bond density of the prepared films changed with the number of incident radicals introduced in hydrogen treatment. This suggests that the selective etching by hydrogen radicals occurs on the SiNx:H surface.

1. INTRODUCTION

In the fabrication of thin-film transistors (TFTs) for liquid crystal displays (LCDs), a dry etching method offering a high etch rate and high selectivity is required to obtain high throughput. One method commonly used for dry etching semiconductor devices is the reactive ion etching method (RIE).[1] However, this method makes it difficult to obtain a high selection ratio.

In this paper, we first present a novel high rate selective etching method for a-Si:H which employs a hydrogen microwave afterglow technique.

Next, to clarify how selective etching affects the a-SiNx:H surface, we prepared a-SiNx:H films by intermittent deposition with subsequent H-radical treatment. We then examined the atomic composition (N/Si) and hydrogen-bond density (Si-H and N-H) of the films.

2. EXPERIMENTAL

The experimental apparatus is a stainless steel chamber equipped with a 1/2-inch-diameter quartz discharge tube. A 2.45-GHz microwave is introduced into the discharge tube through a coaxial cable and a microwave cavity surrounding the tube.[2] The substrate temperature is controlled between 15-350°C using a heater and a thermoelectric element.

In measuring the etch rate of a-Si:H and its selectivity against other materials, films made of a-Si:H, a-SiN$_{1.2}$:H, a-SiC$_{0.5}$:H, SiO_2, and of Al were used. These films were prepared by plasma-CVD, microwave afterglow CVD, H-radical CVD and thermal CVD, respectively.

To examine the effect of modifying the surface of a-SiNx:H film surface, ultrathin a-SiNx:H layers were stacked intermittently on a substrate by the NH_3 microwave afterglow method.[2] Hydrogen-radical treatment was carried out between each layer deposition cycle. The film preparation sequence and deposition conditions are shown in Fig. 1 and Table I, respectively. The change in composition (N/Si) and hydrogen-bond density of the film as a function of hydrogen treatment conditions and the layer thickness per deposition cycle were analyzed. The film composition was estimated by ESCA and the hydrogen-bond density by FT-IR.

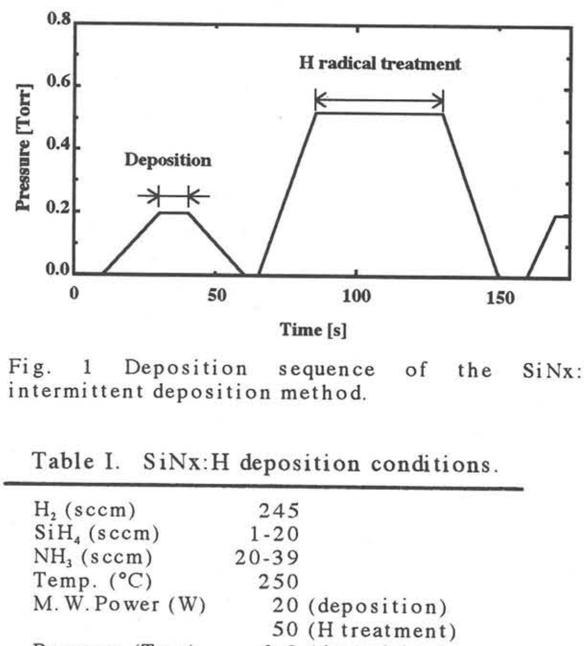

Fig. 1 Deposition sequence of the SiNx:H intermittent deposition method.

Table I. SiNx:H deposition conditions.

H_2 (sccm)	245
SiH_4 (sccm)	1-20
NH_3 (sccm)	20-39
Temp. (°C)	250
M.W. Power (W)	20 (deposition) 50 (H treatment)
Pressure (Torr)	0.2 (deposition) 0.5 (H treatment)

3. RESULTS & DISCUSSION

3.1 High rate selective etching of a-Si:H by hydrogen radical

Figure 1 shows the etch rate of a-Si:H as a function of temperature. The etch rate is less than 2×10^{-4} μm/min when the temperature is below 20 °C and drastically increases as the temperature increases above 20°C, saturating around 100 °C.

A very high a-Si:H etch rate of 2.7 μm/min was obtained at a microwave power of 170 W at 50° C. However, a-SiN$_{1.2}$:H, a-SiC$_{0.5}$:H, SiO_2, and Al were

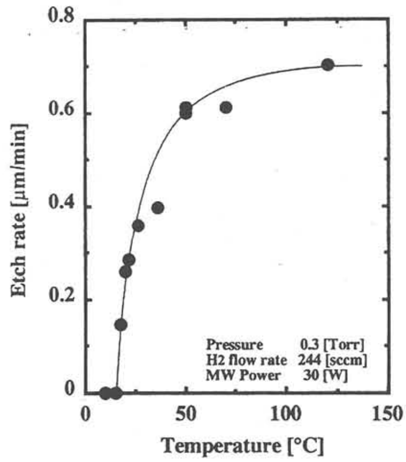

Fig. 2 The etch rate of a-Si:H as a function of temperature.

barely etched below 300 °C, suggesting that high rate selective etching of a-Si:H can be achieved by the microwave hydrogen afterglow method.

Since the strong temperature dependence shown in Fig. 2 cannot be explained by any simple thermally activated process, other processes should be discussed. It has been reported that in mercury-sensitized hydrogen-radical photoetching of a-Si:H, the etch rate decreases with increasing temperature.[3] This temperature dependence is explained by the decrease in the amount of adsorbate supplying H radicals near the film surface with increasing temperature. However, our results differ from these.

Therefore, we propose that SiH_2 or SiH_3 is generated when H-radicals are adsorbed on the film surface and that, below 20°C, they cover the entire film surface, effectively blocking incident H radicals. Above 20°C, incident H radicals diffuse into the film with the assistance of thermal vibration of Si-H bonds or Si-Si bonds. Consequently, mainly SiH_4 molecules are produced and evaporate from the surface. Thus, the etch rate drastically increases with an increase in temperature. We considered that at temperatures above 100°C, the hydrogen supply rate limits the etch rate.

In hydrogen radical etching, all possible H-radicals are inserted into Si-Si bonds, converting them into Si-H bonds. In this way, volatile species such as SiH_4 and Si_2H_6 form and are removed from the surface. The differences in the etch rate between a-Si:H and a-$SiN_{1.2}$:H, and SiO_2 and a-$SiC_{0.5}$:H can be ascribed to the differences in the bonding energies. The bonding energies of Si-N, Si-O, and Si-C are higher than that of Si-H; hence, these bonds are stable against H-radical treatment. Al does not form volatile species with H-radicals.

3.2 Modification effect of a-SiNx:H surface by hydrogen radical

Figures 3 and 4 show the characteristics of the SiNx:H films deposited by intermittent deposition when the source-gas flow ratio of NH_3/SiH_4 is 20/20. The films continuously deposited in this condition are silicon rich and contain many Si-H bonds.

Figure 3 shows the N/Si ratio and hydrogen-bond density of a-SiNx:H as a function of the microwave power during hydrogen-radical treatment. With increasing microwave power, the N/Si ratio increases and the Si-H bond density decreases. This suggests that these characteristics change according to the

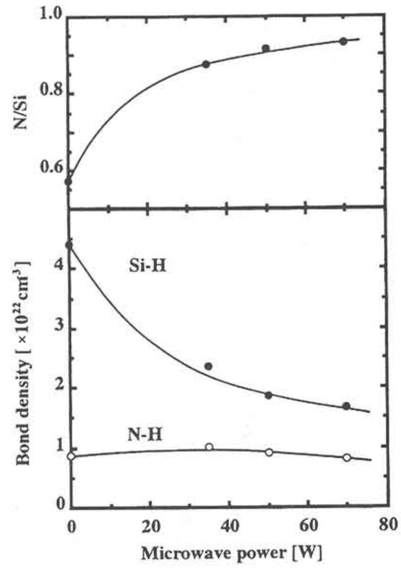

Fig. 3 The N/Si and hydrogen-bond density of a-SiNx:H prepared by intermittent deposition as a function of microwave power during hydrogen-radical treatment. NH_3/SiH_4=20/20

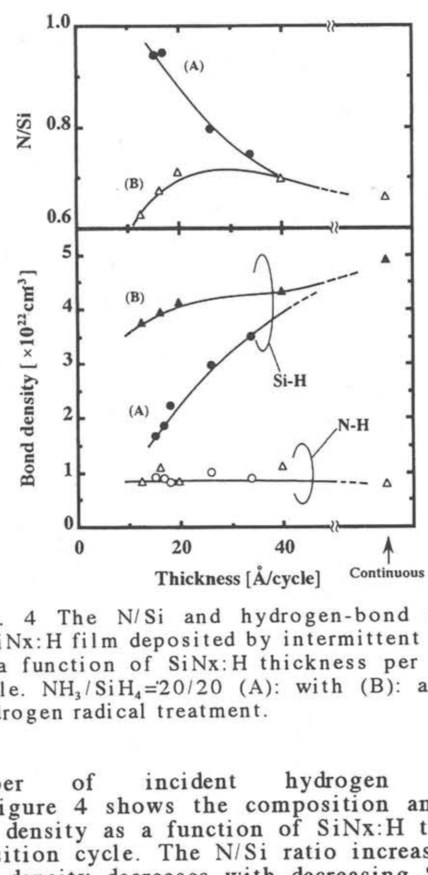

Fig. 4 The N/Si and hydrogen-bond density of a-SiNx:H film deposited by intermittent deposition as a function of SiNx:H thickness per deposition cycle. NH_3/SiH_4=20/20 (A): with (B): and without hydrogen radical treatment.

number of incident hydrogen radicals.

Figure 4 shows the composition and hydrogen-bond density as a function of SiNx:H thickness per deposition cycle. The N/Si ratio increases and Si-H bond density decreases with decreasing SiNx:H film thickness per deposition cycle. Moreover, those effects are enhanced when the film is thinner than 30 Å. This indicates that surface modification with hydrogen radicals has a greater effect when using this deposition method. This means that the hydrogen radicals selectively etch surplus Si atoms on the SiNx:H surface by forming Si-H bonds such as SiH_4 or Si_2H_6.

Figures 5 and 6 show the film deposited by intermittent deposition when the source-gas flow ratio of NH_3/SiH_4 is 39/1. Films continuously deposited in this condition are nearly stoichiometric and contain many N-H bonds.

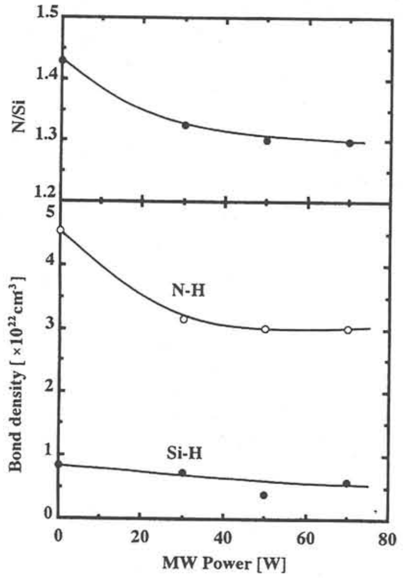

Fig. 5. The N/Si and hydrogen-bond density of the a-SiNx:H prepared by intermittent deposition as a function of microwave power during hydrogen-radical treatment. $NH_3/SiH_4=39/1$

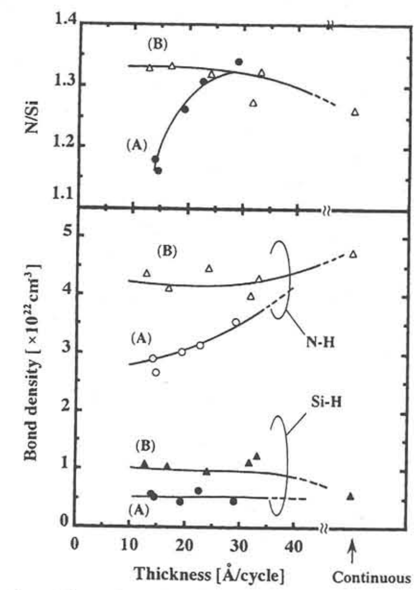

Fig. 6. The N/Si and hydrogen-bond density of a-SiNx:H film deposited by intermittent deposition as a function of SiNx:H thickness per deposition cycle. $NH_3/SiH_4=39/1$ (A): with (B): and without hydrogen radical treatment.

Figure 5 shows the N/Si composition and hydrogen-bond density of a-SiNx:H as a function of microwave power during hydrogen-radical treatment. The N/Si ratio decreases with increasing microwave power. Figure 6 shows the N/Si composition and hydrogen-bond density as functions of SiNx:H thickness per deposition cycle. Both the N/Si ratio and the N-H bond density decreases with decreasing film thickness per deposition cycle. As before, the effects are enhanced when the film is thinner than 30 Å. From these results, we conclude that hydrogen radicals remove N atoms from the a-SiNx:H film surface when it contains many N-H bonds by forming N-H bonds, such as NH_3.

The order of bonding energy is Si-Si<Si-H<Si-N <N-H<H-H.[4] The stability of the film against hydrogen radicals can be explained by these differences in bonding energy. In Si-rich film, hydrogen radicals easily cut the Si-Si bonds and the surplus Si atoms forming Si-H bonds are removed as SiH_4 or Si_2H_6. However, Si-N and N-H bonds are more stable than Si-Si bonds against hydrogen radicals. As a result, Si-N bonds are left and N/Si ratio increases with an increase in incident hydrogen radicals.

The film containing many N-H bonds, contains predominantly $N\text{-}H_2$[5] and the $Si\text{-}NH_2$ structures are unstable against hydrogen radicals. In this case, hydrogen radicals cut the Si-N bonds, and the N atoms which form $N\text{-}H_2$ bonds are removed as NH_3.

Some hydrogen dilution effects of a-SiNx:H deposition have been reported.[6-7] However, the mechanism of this effect is not clear. Our results suggest that selective etching by hydrogen radicals contributes to the surface reactions brought on by deposition and this, in turn, affects the Si-H or N-H content and film composition.

4. CONCLUSION

High rate selective etching of a-Si:H was achieved by using a hydrogen microwave afterglow method. In this method, we clarified the effects of modifying an a-SiNx:H surface by hydrogen radicals. In a Si-rich film surface, containing many Si-H bonds, Si atoms forming Si-H bonds are removed by hydrogen radicals as SiH_4. On the other hand, on the near stoichiometric film surface, containing many N-H bonds, N atoms forming N-H bonds are removed by hydrogen radicals as NH_3. This clarifies that selective etching by hydrogen radicals is the mechanism of the surface reactions, affecting the Si-H or N-H bond density and N/Si composition.

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