Dependence of wet etch rate on deposition, annealing conditions and etchants for PECVD silicon nitride film*

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Abstract: The influence of deposition, annealing conditions, and etchants on the wet etch rate of plasma enhanced chemical vapor deposition (PECVD) silicon nitride thin film is studied. The deposition source gas flow rate and annealing temperature were varied to decrease the etch rate of SiN_x:H by HF solution. A low etch rate was achieved by increasing the SiH_4 gas flow rate or annealing temperature, or decreasing the NH_3 and N_2 gas flow rate. Concentrated, buffered, and dilute hydrofluoric acid were utilized as etchants for SiO_2 and SiN_x:H. A high etching selectivity of SiO_2 over SiN_x:H was obtained using highly concentrated buffered HF.

Key words: plasma enhanced chemical vapor deposition; silicon nitride; HF solution; etch rate
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1. Introduction

As an extensively used dielectric in micro-electro-mechanical systems (MEMS), plasma enhanced chemical vapor deposition (PECVD) silicon nitride can play a very important role in MEMS devices. Although PECVD SiN_x:H has been extensively investigated by many researchers, requirements of film properties vary from device to device. For some applications utilizing SiN_x:H as the structural and isolation layers, and SiO_2 as sacrificial layer, it is very desirable to obtain a high SiO_2/SiN_x:H etching selectivity.

The etching rate of SiN_x:H in HF-based solutions strongly depends on the Si/N ratio[1−3] and on the hydrogen concentration of the film[1,4], in terms of Knotter's reaction mechanism for SiN_x:H and hydrofluoric acid (HF)[5]. Adjusting the deposition conditions can tune the film composition, while thermal treatment after deposition can decrease the H concentration and increase the density of the film, thereby improving the etching resistance of SiN_x:H to HF.

A systematic investigation was carried out to study the hydrofluoric acid etching of SiN_x:H film deposited under various conditions and annealed by rapid thermal annealing (RTA). Different HF-based solutions were also utilized to realize a high SiO_2/SiN_x:H etching selectivity.

2. Experimental

A p-type Si (100) wafer cleaned by standard chemical cleaning procedures was used as the substrate for all the samples. SiN_x:H deposition was performed in a commercial PECVD chamber using 5% silane (SiH_4) diluted in Ar, ammonia (NH_3) and nitrogen (N_2) as source gas. The gas flow rate was varied, while the pressure and substrate temperature were kept at 900 mTorr and 300 ° C, respectively. Ellipsometry was used to determine the film thickness and refractive index. The etching in HF-based solution was performed at room temperature. The film thickness was measured before and after etching the sample. Then the etch rate was calculated from the thickness difference divided by the etching time.

RTA was performed between 650 and 900 °C in N_2 atmosphere. Then both the as-deposited and annealed samples were etched in concentrated hydrofluoric acid.

Concentrated hydrofluoric acid, buffered hydrofluoric acid (BHF), and dilute hydrofluoric acid (DHF) were used as etchants for SiN_x:H and SiO_2. Deposition parameters for all the SiN_x:H films are listed in Table 1, and the SiO_2 film was deposited at 300 °C, 900 mTorr, 380 kHz, 30 W, $SiH_4/N_2O/N_2$ = 150/1420/390 sccm. The film stress was measured by a profilometer (Dektak 8). The BHF was produced from 1 part 49% hydrofluoric acid and *n* parts 40% ammonium fluoride (NH_4F) by volume, *n* being 1, 3, 5. The DHF was produced from 1 part 49% hydrofluoric acid and 1 part water by volume.

3. Results and discussion

The deposition process consists of gas ionization and dissociation, gas phase reaction or surface insertion of Si- and N-containing radicals, and hydrogen elimination[6,7]. High gas flow rate and power lead to high plasma density. Collisions take place in a dark space, and the ion energy decreases with increasing pressure. A low frequency power results in ions with high energy, while a high frequency power could lead

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Table 1. Deposition parameters for the SiN_x:H films.

Sample	SiH_4 (sccm)	NH_3 (sccm)	N_2 (sccm)	Power (W)	Frequency (kHz)
LF1	750	30	1200	250	380
LF2	780	30	1200	250	380
LF3	800	30	1200	250	380
LF4	840	30	1200	250	380
LF5	900	30	1200	250	380
LF6	800	20	1960	250	380
LF7	800	25	1960	250	380
LF8	800	30	1960	250	380
LF9	800	40	1960	250	380
LF10	800	50	1960	250	380
LF11, LF12	600	20	1960	150	380
HF1, HF2	600	55	1960	150	13560

to a reduction of the ions' flux and energy.

According to Knotter's research[1], in the reaction between SiN_x:H and HF solution, a silane (Si-NH_2) surface group must be substituted by a fluoride group. It contains several steps: the protonation of the Si-NH_2 to Si-NH_3^+, breaking of the Si–N bond and elimination of NH_3, and a subsequent addition of F^- or HF to the vacant surface site to form a Si–F bond. Then the other Si–N bonds in the silicon nitride network break and Si–F bonds form via a nucleophilic substitution reaction with lower activation energies. Monofluorides are the main active species for etching of SiN_x:H. When Si–H and N–H bonds exist, they break the silicon nitride matrix, therefore a nucleophilic substitution reaction can take place without protonating the Si-NH_2 and breaking the Si–N bond beforehand, which is the rate-limiting step for SiN_x:H etching reactions. Thus the etch rate increases extensively with H concentration.

The etching of SiO_2 is mainly done through attaching the proton of HF_2^- to a free electron pair of oxygen atoms, polarizing the Si–O bond and bringing a fluoride close to the Si atom. The Si–O bond breaks and a new Si–F bond forms at the same time.

3.1. Deposition

By adjusting the source gas flow ratio, Si-rich or N-rich SiN_x:H films can be obtained. The Si/N ratio of SiN_x:H films is the determining factor for the etching resistance. The Si/N ratio can normally be estimated by measuring the refractive index (n) of SiN_x:H films and is calculated using an empirical expression[8, 9],

$$\frac{[\mathrm{N}]}{[\mathrm{Si}]} = \frac{4(n_{\text{a-Si:H}} - n)}{3(n + n_{\text{a-Si:H}} - 2n_{\text{a-Si}_3\text{N}_4})} = \frac{4(3.3 - n)}{3(n - 0.5)}, \quad (1)$$

where $n_{\text{a-Si:H}} = 3.3$ and $n_{\text{a-Si}_3\text{N}_4} = 1.9$ are the refractive indices of a-Si:H and nearly stoichiometric a-Si_3N_4.

Figures 1 and 2 show the dependence of the etch rate and the refractive index on SiH_4 and NH_3 gas flow rates, respectively. Increasing the $SiH_4/(NH_3+N_2)$ ratio will increase the Si/N ratio in the deposited film. As can be seen from Fig. 1, when the SiH_4 gas flow rate increases, the reflective index

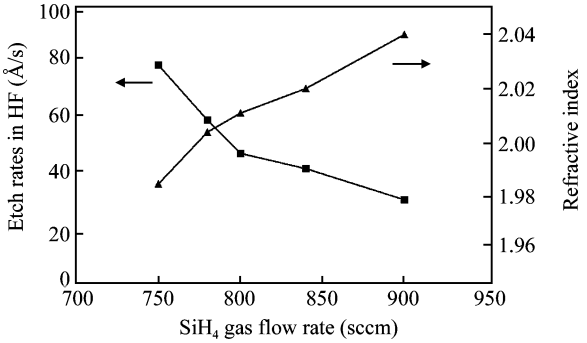

Fig. 1. Influence of SiH_4 gas flow rate on the refractive index n and the etch rate of SiN_x:H.

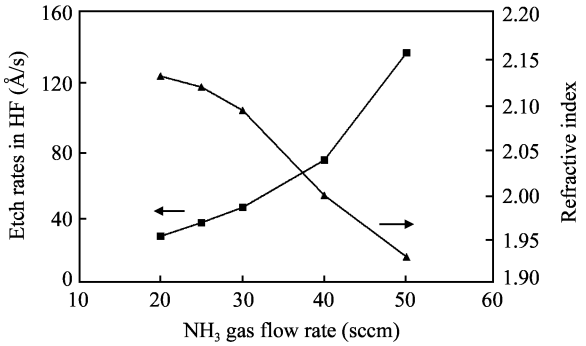

Fig. 2. Influence of NH_3 gas flow rate on the refractive index n and the etch rate of SiN_x:H.

increases, and the etch rate decreases. This can be explained by the Si–Si bond concentration increasing with n; the surface Si are oxidized to SiOH before they are etched, making the etching more complex and much slower[5]. In contrast, increasing the NH_3 gas flow rate decreases the refractive index and raises the etch rate, as shown in Fig. 2. In addition, the high NH_3 gas flow rate results in more N–H bonds inserted in the deposited film, which can largely accelerate the etch reaction.

The Si/N ratio depends on power, pressure and frequency due to the higher dissociation energy of N_2 and NH_3 than that of SiH_4. The increased dissociation of N_2 and NH_3 at a higher power will supply more reactive nitrogen precursors, thus more nitrogen radicals will incorporate in the film. The

Table 2. Etch rates and etch rate ratios of SiO_2 and SiN_x:H in HF-based solutions.

	Etch rate (Å/s)			Etch rate ratio	
	SiO_2	SiN_x:H (LF12)	SiN_x:H (HF2)	SiO_2/SiN_x:H (LF12)	SiO_2/ SiN_x:H (HF2)
49% HF	1276.6	24.3	128.8	52.5	9.9
1 : 1 BHF	600	10.8	51.6	55.6	11.6
1 : 3 BHF	90.9	3.0	13.8	30.3	6.6
1 : 5 BHF	34	1.7	8.9	20	3.8
1 : 1 DHF	269.5	11.7	63.2	23.0	4.3

ion energy decreases with increasing pressure, which leads to lower dissociation degree of the reacting species, especially nitrogen precursors, and results in a higher Si/N ratio. Furthermore, at higher frequency, the fast alternating electric field leads to lower ion flux and energy, and thus is favorable for formation of the Si-rich film.

3.2. Annealing

There is a significant amount of hydrogen incorporated in the PECVD SiN_x:H film in the form of Si–H, N–H bonds and unbonded H. Hydrogen concentration decreases with increasing deposition or annealing temperature.

Several reactions may take place during the annealing[10–13].

$$\text{Si–H} + \text{N–H} \rightarrow \text{Si–N} + \text{H}_2, \quad (2)$$

$$\text{Si–H} + \text{Si–H} \rightarrow \text{Si–Si} + \text{H}_2, \quad (3)$$

$$\text{Si–NH–Si} + \text{Si–NH–Si} \rightarrow \text{Si–N–Si}_2 + \text{NH}_2. \quad (4)$$

Annealing at high temperature breaks the Si–H and N–H bonds, releases hydrogen and forms new Si–N or Si–Si (for Si-rich film) bonds, or breaks the Si–H and N–H bonds without healing. It is also possible that the near-neighboring SiN–H groups react to form NH_3 or ammonia fragments, such as NH_2. The unbonded H may react with the hanging Si or N to form new Si–H and N–H bonds at the same time, which may influence the release of H in a certain temperature range. At higher temperature, H desorption is dominant, which causes a dramatic decrease in H concentration. The film shrinks during annealing, and the film stress changes towards tensile.

Figure 3 presents the etch rates of the SiN_x:H film (sample HF1 and LF11) versus the annealing temperature. Annealing was performed between 650 and 900 °C for 30 s. The etch rates were measured before and after annealing in concentrated HF. The SiN_x:H films deposited at low frequency (380 kHz) had compressive stress, and the etch rate fell from 24.3 to 4.6 Å/s after annealing. Conversely, the SiN_x:H films deposited at high frequency (13.56 MHz) showed tensile stress, and the etch rate decreased from 129 to 12 Å /s with increasing temperature, which was about 1/10 of that of the as-deposited film. The lower etch rate for SiN_x:H deposited at low frequency can be explained by reduction of the NH_3 gas flow rate, film densification and Si–H, N–H bonds breaking by more significant ion bombardment than that for high frequency deposition.

Blisters appeared in some films with the compressive stress after annealing, due to the diffusion and accumulation of hydrogen at the film-substrate interface[2]. The higher the annealing temperature, the more blisters appeared. The films with the tensile stress cracked after annealing. The crack started at the film-substrate interface, and extended towards the surface with increasing annealing temperature. This can be explained by the film shrinking after hydrogen desorption.

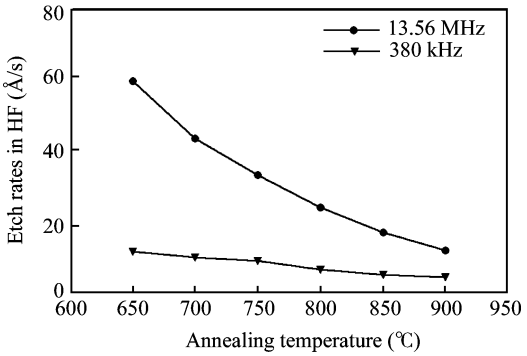

Fig. 3. Etch rates of SiN_x:H deposited at low frequency (380 kHz) and high frequency (13.56 MHz), before and after annealing in concentrated HF.

3.3. Etch rates in HF solutions with different ingredients

Both Knotter[5] and Deckert[14] reported that SiO_2 is preferentially etched over SiN_x:H in high concentration, low temperature and high ionization HF-based solutions. Since SiO_2 and SiN_x:H are mainly etched by difluorides and monofluorides, respectively, it is possible to control the etching selectivity by adjusting the relative ion concentration.

The etch rates of SiN_x:H in concentrated, buffered and dilute HF are summarized in Table 2. The etch rates of both SiO_2 and SiN_x:H increase with increasing HF concentration, with that of SiO_2 increasing more. This results in a higher selectivity for SiO_2 over SiN_x:H etching, since HF_2^- prefers to form in solutions with higher HF concentration. Moreover, we can see that the selectivity of 1 : 1 BHF is slightly higher than the concentrated HF, and much better than the 1 : 1 DHF, because the NH_4F can be decomposed to HF, stabilize the ion concentration and hence the etch rate, and help to shift the fluoride equilibrium towards difluorides.

4. Conclusion

Wet etching of PECVD SiN_x:H films in HF-based solutions is studied in this paper. In order to get a relatively low

SiN_x:H etch rate and high SiO_2/SiN_x:H etching selectivity, three approaches are adopted: optimizing the deposition parameters, annealing, and optimizing the etchant. Increasing the Si/N ratio could extensively decrease the etch rate, which was achieved by increasing the SiH_4 gas flow rate and/or decreasing the NH_3 and N_2 gas flow rate. High temperature RTA released the H and reconstructed the film, causing a tremendous decrease in etch rate. An etch rate as low as 4.6 Å/s was obtained. Changing the HF-based solutions can vary the etch rate of SiO_2 and SiN_x:H, and hence improve the etching selectivity. The 1 : 1 BHF was found to be optimum for this purpose.

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