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Etching of chemically vapour-deposited amorphous Si_3N_4–C composites in HF solution

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Amorphous Si_3N_4–C[Am.CVD-(Si_3N_4)] composites (C: 0.6 to 6 wt %) were prepared by chemical vapour deposition (CVD) using $SiCl_4$, H_2, NH_3 and C_3H_8 gases, and their etching characteristics in 47% hydrofluoric acid (HF) solution were investigated in the temperature range of 25 to 50° C. It was found that the etching rate decreases with increasing carbon content. The etching rate of the Am.CVD-(Si_3N_4–C) composite containing 6 wt % carbon was about 1/40 of the rate for carbon free Am.CVD-Si_3N_4. The activation energies obtained from the temperature dependence of the etching rates were 11 to 17 kcal mol^{-1}, which increased with increasing carbon content. This paper also presents the study on the characteristics of the etched surfaces as well as the carbon state in the Am.CVD-(Si_3N_4–C) composites, and finally the possible etching mechanism is discussed.

1. Introduction

In semiconductor technology, the amorphous Si_3N_4 films have been widely used as diffusion masks, gate dielectrics and passivation films. A particular pattern of the amorphous Si_3N_4 film is usually made by photolithography, in which the plasma dry etching or chemical wet etching using HF or H_3PO_4 is employed. In practice, however, the chemical wet etching is used more often because of its simplicity and ease of handling. The only draw back of this technique is the possible occurrence of undesirable "under-cutting". One of the methods to obtain tapered edges avoiding the under cutting is to control the etching rate of the film in such a way that the etching rate is the fastest at the uppermost and the slowest at the bottommost of the film [1].

The present authors have successfully prepared plates of the amorphous Si_3N_4–C[Am.CVD-(Si_3N_4–C)] composites by chemical vapour deposition (CVD) [2], and have investigated their structures [3] and some of their properties [4, 5]. This paper describes the etching rates of the Am.CVD-(Si_3N_4–C) composites in 47% HF solution in the temperature of 25 to 50° C. The paper also discusses the relationship between the etching rate and the carbon content. The characteristics of the etched surface as well as the carbon state in the Am.CVD-(Si_3N_4–C) composite are also presented. Finally, the etching mechanism is discussed.

2. Experimental procedures

The Am.CVD-(Si_3N_4–C) composites were prepared by chemical vapour despoition (CVD) on directly heated graphite substrates using $SiCl_4$, H_2, NH_3 and C_3H_8 gases. The detailed procedures for the sample preparation have been described elsewhere [2]. The deposition conditions and some properties of the Am.CVD-(Si_3N_4–C) composites are summarized in Table I. The Am.CVD-(Si_3N_4–C) composites were ultrasonically cut to a disc with 5 mm in diameter and shaved to about 1 mm in thickness using a diamond grinder. Then the specimens were metallographically polished using Al_2O_3 pastes and ultrasonically cleaned in acetone. The specimens were then put into polyethylene bottles filled with 47% HF solution and sealed air tight. The temperature of the bottle filled with the HF solution was controlled to within ± 0.02° C of the prescribed temperature in the range of 25 to 50° C by placing it in a constant temperature water bath. The etching rate was obtained by measuring the weight loss of the specimens as a

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TABLE I The deposition conditions and some properties of the specimens. (T_{dep}* = 1300° C, P_{tot}† = 30 torr)

$FR(C_3H_8)$‡ ($cm^3 min^{-1}$)	Density ($g cm^{-3}$)	Carbon content (wt %)	Colour
0	3.00	0	White
40	2.98	0.6	Black
70	2.95	2	Black
100	2.85	6	Black

*T_{dep}: deposition temperature.
†P_{tot}: total gas pressure.
‡$FR(C_3H_8)$: propane gas flow rate.

function of time at a fixed temperature. The maximum time interval of the measurement was 27 h. The resulting etched surfaces of the specimen were observed by using a scanning electron microscope (SEM).

The specimen containing 6 wt % carbon was pulverized to 200 mesh or less. The powder was immersed in the HF solution at 25° C for about 1400 h, and then the characteristics of the residue was studied by an X-ray diffraction, a chemical analysis and a transmission electron microscope (TEM).

3. Results and discussion

3.1. Etching rate

Fig. 1 shows the time dependence of the weight loss for the specimens etched in the HF solution at 25° C. As it is shown clearly in Fig. 1, every specimen loses its weight linearly with time. The etching rates were obtained from the slopes of these straight lines. The small weight decrease during the initial one hour may be explained by the presence of the oxide or oxynitride layer on the specimen surface. Fig. 2 indicates the relationship between the carbon content and the etching rate. The etching rate of the Am.CVD-(Si_3N_4–C) composite containing 6 wt % carbon was about 1/40 times smaller than that of the Am.CVD-Si_3N_4. The Table II lists the available data [6–11] on the etching rates measured at room temperature in concentrated HF solution for the Am.CVD-Si_3N_4 prepared at relatively high deposition temperatures. In Table II the unit of the etching rate is represented by ($nm\,min^{-1}$). The etching rates of the Am.CVD-Si_3N_4 obtained in the present work are 8 to 50 times larger than the values reported [6–11]. The reason for this difference may be due to the stress corrosion as will be discussed in Section 3.2.

Fig. 3 shows the Arrhenius plot of the etching rates. The etching rates for all specimens examined increase with increasing temperature. The activation energies required for the etching of the Am.CVD-Si_3N_4 and the Am.CVD-(Si_3N_4–C) composite containing 6 wt % carbon were 11 and 17 $kcal\,mol^{-1}$, respectively. The activation energy slightly increases with increasing carbon content. Table III summarized the previously reported values of activation energy required for etching of the Am.CVD-Si_3N_4 [1, 12–15], and the results from the present work. The values obtained in the present work are almost in agreement with those reported earlier [1, 12–15]. Because only a few $kcal\,mol^{-1}$ of activation energy is usually associated with the diffusion process in solution [16],

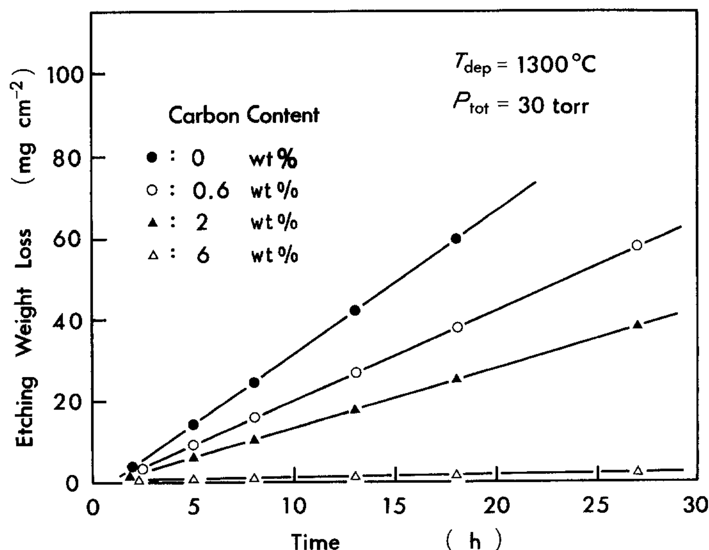

Figure 1 Time dependence of the weight loss by the etching (at 25° C).

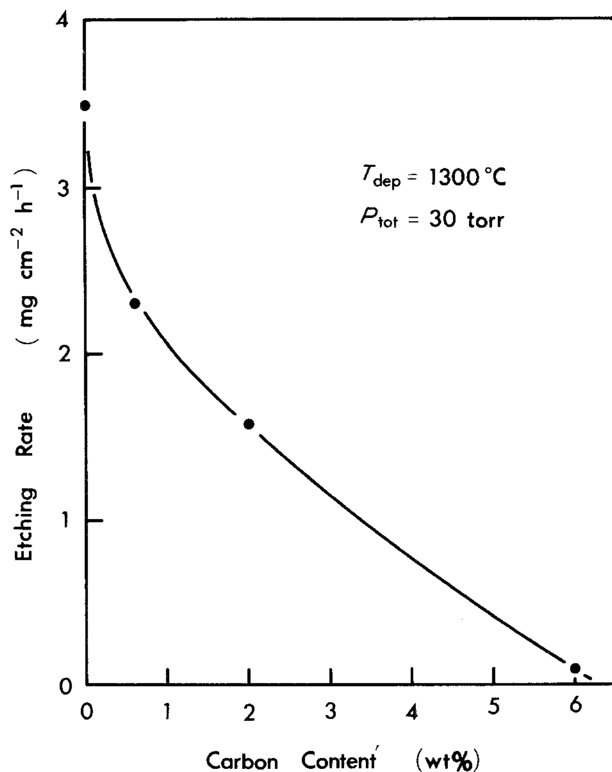

Figure 2 The effect of the carbon content on the etching rate (at 25° C).

the value of activation energy of 11 to 17 kcal mol^{-1} obtained in the present work may better correspond to the chemical reactions at the Si_3N_4 surfaces rather than to the diffusion process. In addition, the value of the activation energy should be independent of the carbon content if the diffusion process in solution is the rate-determining step. Deckert [1] reported that an intermediate hydrogen-bonded species may contribute to the etching mechanism of the Si_3N_4. Thus, it can be speculated that the activation energy obtained in the present work correspons to a chemical reaction such as adsorption of HF molecule or HF_2^- ion at the Si_3N_4 surface.

3.2. Observation of etched surface

Fig. 4 shows the scanning microscopic view of surface of the Am.CVD-Si_3N_4 after etching of 18 h at 25° C. Fig. 4b is a higher magnification of Fig. 4a. Many hairline cracks are visible on the etched surface. Since these hairline cracks were not observed on the original surface, it is concluded that these cracks were formed during the etching process. Grieco *et al.* [11] also reported the similar cracks on the Am.CVD-Si_3N_4 surface etched by water–amine–pyrocatechol system, and they observed the further growth of new cracks as etching proceeded. They explained this formation of cracks as a result of strain release by preferential

TABLE II Etching rates of Am.CVD-Si_3N_4. Etchant: concentrated HF solution. Etching temperature: room temperature

Deposition temperature (° C)	Reactants for CVD	Etching rate (nm min^{-1})	Reference
900	$SiCl_4 + NH_3$	24	6
1000	$SiH_4 + N_2H_4$	15	7
1000	$SiH_4 + NH_3$	4–8	8
1000	$SiH_4 + NH_3$	12	9
1200	$SiH_4 + NH_3$	7–9	10
1225	$SiCl_4 + NH_3$	8	11
1300	$SiCl_4 + NH_3$	190	Present work
1300	$SiCl_4 + NH_3 + C_3H_8$*	5.2–130	Present work

*Si_3N_4–C composites

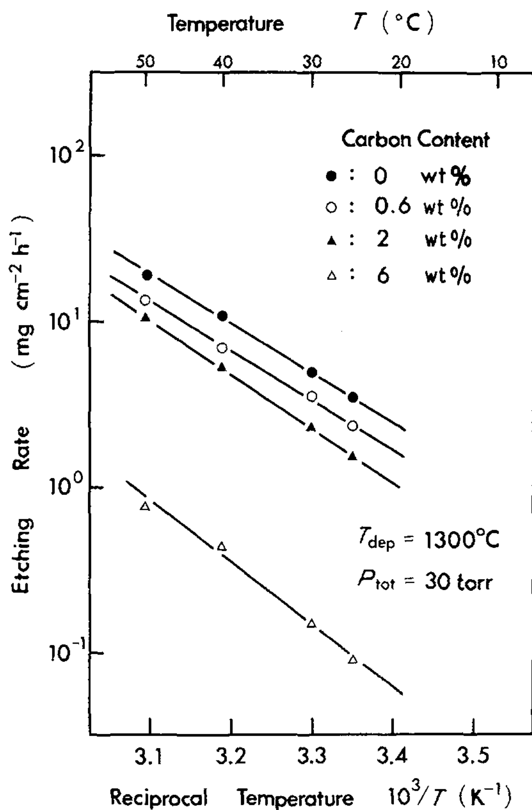

Figure 3 Arrhenius plot of the etching rate.

stress corrosion. The cracks observed in the present work may also be due to the stress corrosion as pointed out by Grieco *et al.* [11].

Figs. 5 and 6 show the specimen surfaces after etching of 18h at 25° C for the Am.CVD-(Si_3N_4–C) composites containing 0.6 and 6 wt% carbon, respectively. Some pores are observed on the etched surface of the Am.CVD-(Si_3N_4–C) composite containing 0.6 wt% carbon. No pores but a large number of cones are observed on the etched surface of the Am.CVD-(Si_3N_4–C) composite containg 6 wt% carbon. These cones appeared on the surface after the etching process may reveal the microstructure formed during the deposition process.

Bohg [17] prepared Am.CVD-Si_3N_4 thin film containing carbon at T_{dep} = 600 to 1100° C using $SiH_4 + NH_3 + C_3H_8$ gases and measured the internal stress in the film at 800° C. The value of the internal stress was reported as about 0.3×10^9 dyne cm^{-2} which is only about 60% of the value normally encountered. This fact suggests that the internal stress in the present Am.CVD-(Si_3N_4–C) composites decreases with increasing carbon content. The cause of much higher internal stress in the Am.CVD-Si_3N_4 not containing carbon may be related to the fact that the deposition rate of the Am.CVD-Si_3N_4 is 100 to 1000 times larger than those of previous films.

3.3. State of the carbon

The Am.CVD-(Si_3N_4–C) composite containing 6 wt% carbon was pulverized and completely dissolved in the HF solution. After the evaporation of the solvent, the residue was divided into two parts; one insoluble and the other soluble in the water. The insoluble residue was observed by TEM as shown in Fig. 7. The electron diffraction pattern and the chemical analysis both revealed that the residue is an amorphous carbon. Fig. 7 shows that amorphous carbon in the Am.CVD-(Si_3N_4–C) composite is circular shaped particles with diameter of about 100 nm. An X-ray diffraction analysis showed that the soluble residue is $(NH_4)_2SiF_6$.

4. Conclusions

The etching rates of the amorphous CVD-Si_3N_4 and the amorphous Si_3N_4-C[Am.CVD-(Si_3N_4–C)] composites prepared by chemical vapour depo-

TABLE III Activation energies of etching of Am.CVD-Si_3N_4

Reactants for CVD	Etching temperature (° C)	Etchant	Activation energy (kcal mol^{-1})	Reference
$SiCl_4 + NH_3$	25–60	$HF + C_3H_8O_3 + H_2O$	14	1
$SiCl_4 + NH_3$	70–90	$HF + HNO_3 + H_2O$	12.5	12
$SiH_4 + NH_3$	15–60	$HF + NH_4F + H_2O$	15	13
$SiH_4 + NH_3$	25–90	$HF + H_2O$	13.6	14
$SiH_4 + NH_3 + AlCl_3$*	40–180	$H_3PO_4 + H_2O$	14–19	15
$SiCl_4 + NH_3$	25–50	$HF + H_2O$	11	Present work
$SiCl_4 + NH_3 + C_3H_8$†	25–50	$HF + H_2O$	13–17	Present work

*Si_3N_4–AlN composites.
†Si_3N_4–C composites.

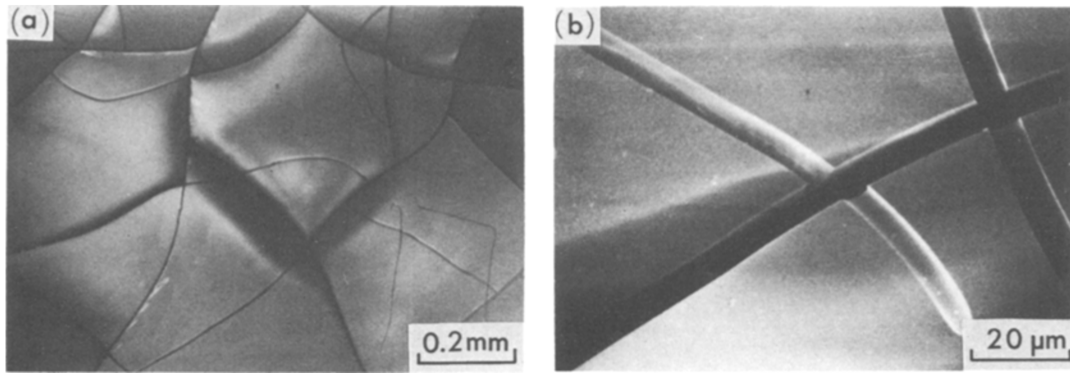

Figure 4 The surfaces of the Am.CVD-Si_3N_4 etched at 25° C for 18 h. (b) is a higher magnification of (a).

sition were measured in the range of 25 to 50° C using 47% HF solution, and the following results were obtained.

1. The weight loss by etching has a linear relationship with etching time.

2. The etching rate of the carbon free Am.CVD-Si_3N_4 is 5 to 80 times larger than the previously reported values. This may be due to the internal stress contained in the present deposits.

3. The etching rates of the Am.CVD-(Si_3N_4–C) composites decrease with increasing carbon content. Carbon may help release the stress in the composites. The etching rate of the Am.CVD-(Si_3N_4–C) composite containing 6 wt% carbon is about 1/40 times smaller than that of the Am.CVD-Si_3N_4.

4. The activation energy for etching is 11 to 17 kcal mol^{-1}. This values increase with increasing carbon content.

5. The hairline cracks are observed on the etched surface of the Am.CVD-Si_3N_4. These hairline cracks may be caused by the stress corrosion.

6. Some pores are observed on the etched surface of the Am.CVD-(Si_3N_4–C) composites containing 0.6 wt% carbon and a large number of cones are observed for specimen with 6 wt% carbon.

7. The carbon in the Am.CVD-(Si_3N_4–C) composite is amorphous carbon in the shape of circular particles with diameter of about 100 nm.

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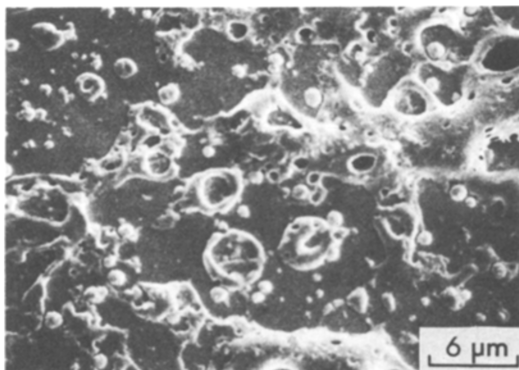

Figure 5 The surface of the Am.CVD-(Si_3N_4–C) composite (C: 0.6 wt%) etched at 25° C for 18 h.

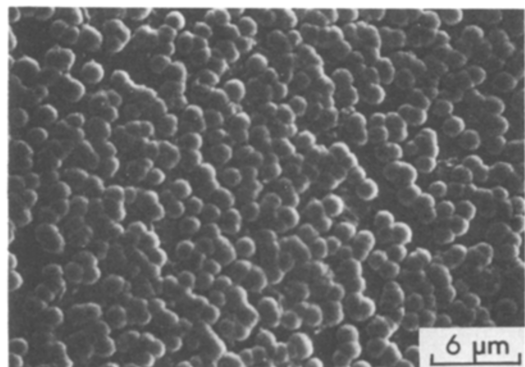

Figure 6 The surface of the Am.CVD-(Si_3N_4–C) composite (C: 6 wt%) etched at 25° C for 18 h.

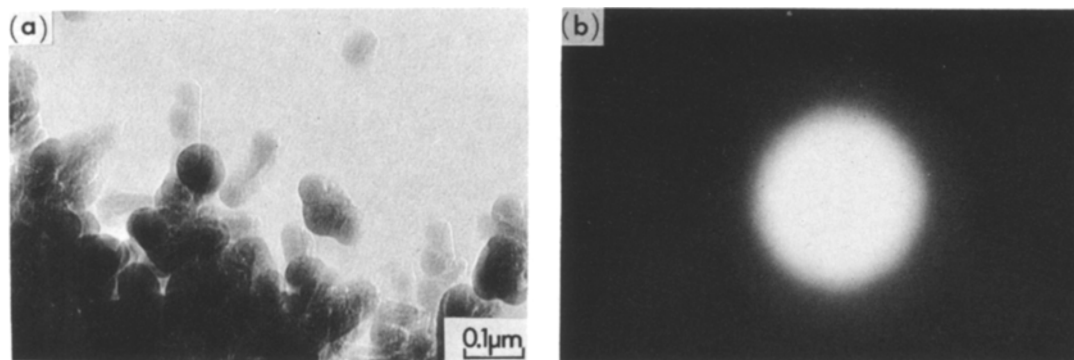

Figure 7 Electron micrograph (a) and electron diffraction pattern (b) of amorphous carbon in the Am.CVD-(Si_3N_4–C) composite.

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