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# Relationship between bonding characteristics and etch-durability of amorphous carbon layer

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ABSTRACT

In the semiconductor industry, amorphous carbon layer (ACL) is widely used as a mask during the etching process. Recent advances in patterning require masks with better etch-durability. To develop such mask, it is essential to understand the relationship between the chemical composition and the etch-durability of the mask. In this work, the relationship between the bonding nature of ACL films and their etch-durability is studied. The bonding characteristics were measured by Fourier transform infrared spectroscopy and the ACL films were deposited under various conditions to observe the change in bonding characteristics. The experimental results show that the ratio between carbon–carbon and carbon–hydrogen bonding is correlated to the etch-durability of ACL film and it is found to be universal under various conditions. Based on this result, an indirect, nondestructive method to determine the etch-durability of the ACL is proposed.

## 1. Introduction

Patterns in the semiconductors are getting finer due to the industrial advantage with smaller devices. In recent days, researches on patterns under 20 nm are being actively conducted. Since previous semiconductor process cannot produce such fine patterns, novel processes are being developed.

The mask is especially critical to produce such fine patterns. Amorphous carbon layer (ACL) is one of the important materials used in the semiconductor industry as a mask in various applications: semiconductor, biology, hard coating, anti-corrosion, solar cells, and organic light emitting diode touch panels [1]. In the semiconductor industry, ACL is widely used as a mask in the etching process due to its chemical stability and comparably high film density. However, mask with better etch-durability than the current typical ACL is essential in order to produce finer patterns.

During the etching process, a certain amount of the mask is lost due to ion bombardment. Thus, the mask must have a low etch rate in order to carry out the process correctly. One way to overcome this problem by simply is using a thicker mask. However, this method is inefficient in terms of process time and cost and also causes problems such as the etching selectivity which damages the substructures. Thus, the fundamental and desirable solution for this problem is to develop and use a mask with high etch-durability.

In order to increase the etch durability of the mask, some studies have been done on using diamond-like carbon (DLC) as a candidate to replace the currently used ACL. It is reported that incorporation of Si in the DLC allows better etch durability than ACL film [2]. However, crystallization and adding another element to the system can make the process complicated and cause uniformity problems since using Si incorporated DLC will require uniform distribution of Si and uniform crystallization of the film. Furthermore, DLC film is not appropriate as mask for some manufacturing process such as photo-masking because of its optical characteristics. Thus, increasing the etch-durability of the currently used ACL is a more practical solution for this problem.

To improve the etch-durability of a film, it is important to understand and control the film's chemical composition. How the elements of the films are bonded can influence the chemical properties, which can change the etch durability of the film.

In this research, chemical bond analysis using Fourier transform infrared (FT-IR) spectroscopy is used to measure the characteristics of the ACL films. The films were deposited under various conditions in order to control their chemical characteristics and etch-durability. Analysis utilizing FT-IR spectroscopy is widely used to study the bonding characteristics of ACL in many researches for various applications [1–8]. However, the same measured results could lead to different interpretations depending on how the data was interpreted. Also, no report has been made on the relationship between the bonding characteristics measured by FT-IR spectroscopy and etch-durability of ACL. There are some reports that mention the relationship between the physical characteristics of the film and FT-IR measurements but these do not discuss the etch-durability. Report by Ilhyun Jung shows how the deposition characteristics affect the bonding characteristics measured by FT-IR. However this report does not relate the bonding characteristics to the mechanical properties and does not mention the etch-durability of the film [9].

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The density of the ACL film is also closely related to the etch durability of the film. The relationship between the film density and the bonding characteristics has been reported by P.C. Kelier and other researchers. However, these reports are only restricted to the bonding characteristics of carbon: sp1, sp2 and sp3 [1,10–13]. Moreover, the film density and the fraction of sp3 bonding do not correlate to etch other when atoms other than carbon, such as hydrogen are incorporated in the film. Increasing the content of hydrogen increases the portion of sp3 bonding while reducing the film density [14–16]. Thus there is no clear method to determine or predict the etch-durability by analyzing the orbital bonding of the film.

In this work, a method to determine the etch-durability of ACL using FT-IR spectroscopy is proposed. Various deposition conditions were used to fabricate the ACL films and the bonding characteristics of the samples were measured by FT-IR spectroscopy and etch-durability were evaluated by measuring thickness of the film. The ratio between carbon–carbon bonds and carbon–hydrogen bonds is compared to an actual etch-durability evaluation using an etching process. The relationship between the bonding ratio and the etch-durability is linear in the process of window of this experiment.

## 2. Experimental procedure

### 2.1. Experimental equipment configurations and experimental methods

Schematic of the experimental equipment is shown in Fig. 1. Plasma enhanced chemical vapor deposition (PECVD) was used to deposit the ACL films. Other methods to deposit ACL films are available [4–7] but PECVD is used in this research since it is a typical method to deposit ACL films in the semiconductor industry. The experimental equipment is a based on Telia 300, a CVD system of TES Co., Ltd. A stainless steel vacuum chamber was used as a reactor. A showerhead was installed on the top part of the chamber in order to distribute the process gas evenly and a heater was installed on the bottom part in order to heat the wafer. Radio frequency of 13.56 MHz (APEX digital 5708009, Advanced Engineering Co.) was applied to the metal mesh within the heater and aluminum alloy showerhead acted as a susceptor. Plasma was generated between the heater and the showerhead in order to deposit ACL films on Si wafer. 300 mm diameter Si wafer was used as a substrate and in order to obtain a uniform deposition, the size of the showerhead and the heater used in this experiment were slightly larger than the wafer.

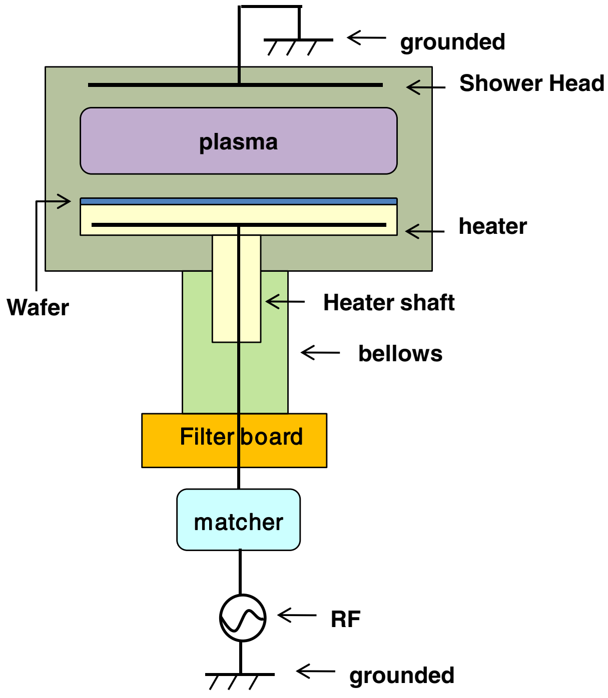

**Fig. 1.** Experimental setup.

To deposit an ACL film, acetylene ($C_2H_2$) gas was used as the source for carbon. Ar and He gas was used to discharge the plasma and $C_2H_2$ was added in order to obtain a stable PECVD deposition. The temperature of the wafer was maintained at 300 °C by heater throughout the experiment.

Etching on the deposited films was processed at the Nano-fab center in KAIST (Korea Advanced Institute of Science and Technology). By etching the films using $CF_4$ gases, the film loss using ACL as a mask in a typical process could be inferred indirectly. The thickness of the film before and after the etching process was measured in order to evaluate the film loss. The thickness of the film was measured using an ellipsometer (M-2000, J.A. Woolam Co.). The mean square error with general oscillator model was under 5 Å and the thickness was also confirmed by scanning electron microscope (S-4800, Hitachi) images with 10 kV of operating voltage.

The chemical bonding characteristics of the deposited films were measured using FT-IR spectroscopy (Nicolet 6700, Thermo Electron Co.). The areas of the peaks in interest were calculated by using OMNIC software that was supplied with the FT-IR equipment.

### 2.2. Experimental details

In this research, ACL films were deposited under various conditions in order to obtain films with different chemical characteristics and etch-durability. The deposition rates of the films were all different due to the various parameters. Thus, the deposition time was set so that the samples will have similar thickness during this research. The similar thickness of the films allows direct comparison between the samples with FT-IR or etching.

Table 1 shows the experimental condition of the first experiment. The ratios of $C_2H_2$, the carbon source in ACL, to other process gases were changed. Other process parameters are kept constant in the experiment. In the second experiment, the RF power applied to discharge the plasma was changed. The other parameters were kept constant, while applied RF power were varied from 800 W to 1600 W.

## 3. Results and discussion

### 3.1. Analysis of etch-durability according to the deposition conditions

In the experiment, ACL films were deposited on Si wafers using PECVD system. The ACL thin film consists mainly of various forms of carbon–carbon($C{=}C$) bonding. However, the small amount of carbon–hydrogen($C-H_x$) bonding influences the film's property as much as the carbon–carbon bonding. The incorporation of hydrogen in the ACL film is unavoidable due to the nature of the deposition system and the gas used. The gas source typically used to deposit carbon film consists of carbon and hydrogen (benzene, acetylene etc.). Thus, in order to deposit pure carbon film, other methods – such as sputtering using graphite source – has to be used instead of PECVD [1]. In this work, compounds $C_2H_2$ and $C_6H_{12}$ were used to deposit the ACL film.

**Table 1**
$C_2H_2$ ratio experiment conditions.

| | | | | |
|---|---|---|---|---|
| Temperature (°C) | 300 | | | |
| Pressure (Pa) | 133 | | | |
| Ar + He (sccm) | 520 | | | |
| $C_2H_2$ (sccm) | 40 | 80 | 120 | 160 |