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Characterization of BCN film after wet process for interconnection integration

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Abstract

In this study, we investigate the influence of the wet chemical processes involved in the chemical treatment of boron carbon nitride (BCN) films deposited by plasma-assisted chemical vapor deposition (PACVD). BCN film is expected to be a low dielectric constant (low-K) material useful in fabricating future generation LSI devices. BCN film with less than 10% oxygen was hardly etched. The etching rate of the BCN film with an oxygen composition ratio more than 10% depends on the pH of the solution. The relationship between the film etching rate and the atomic bonds in BCN film is also investigated using XPS and FTIR. It was found that the BCN films without C–O and B–O bonds are not etched by acid and alkaline solutions. Therefore, suppression of oxygen concentration in the BCN film is important for LSI integration.

Keywords: BCN; LowK; Low dielectric constant; Interconnection; Wet process; XPS; FTIR

1. Introduction

As silicon integrated circuit devices are scaled down below 45 nm, millions of transistors can be assembled on a single chip, which results in an increase in signal transmission time (i.e., RC delay), power consumption, and wire cross talk between multilevel interconnects. These can curtail the benefits of interconnection scaling. Reducing the time delay of ultralarge-scale integrated circuits (ULSI) requires low resistance interconnection materials and interlayer films with a low dielectric constant.

Recently, effort has been devoted to the development of a new low-K material with a dielectric constant lower than 2. For 45-nm node technology and beyond, the primary investigations have been conducted for materials with a SiO-based porous structure. However, most porous low-K films have some serious issues, such as poor hardness and incorporating water into the porous materials.

Boron carbon nitride (BCN) is a well-known material with a hardness >20 GPa [1] Moreover, BCN films composed of N atoms with high electronegativity have a low dielectric constant, in spite of their non-porous structure. Although the investigations revealed that porous films reduce the K-value, we have achieved a dielectric constant as low as 1.9 for BCN films without the pores [2]. There have been some reports of inorganic films, such as carbon nitride (CN) and BCN in which a dielectric constant as low as 2 is realized [3,4].

We have also researched the device applications of BN films deposited by a remote plasma-assisted chemical vapor deposition (PACVD) method. BN films deposited by PACVD have had serious issues, such as cracking and film peeling off the substrate. It has been found that adding carbon atoms to BN films is effective in resolving these issues [5]. No physical change occurs for BCN film with a carbon composition ratio larger than 18%, even after it is wet treated with deionized water (DIW).

Wet processes, such as polymer removal, photo resist, CMP and electro chemical plating are required in the interconnection process, as shown in Fig. 1. Therefore, it is important to investigate the influence of wet chemicals on the BCN film. We determined that the wet chemical influence of BCN film decreases with a decrease in the oxide composition ratio.

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2. Experimental procedure

BCN films were deposited by plasma-assisted chemical vapor deposition (PACVD) at 390 °C [2]. The substrate was set and source gases were introduced into the quartz reactor. Boron trichloride (BCl_3), methane (CH_4), and nitrogen (N_2) were used as source gases. A turn coil was installed around the quartz reactor, and radio frequency (RF) power of 80 W was supplied to the coil to produce remote N_2 plasma by induction coupling. BCl_3 with hydrogen (H_2) gas were introduced near the substrate. CH_4 was added to N_2 plasma. An external furnace maintained the substrate temperature at 390 °C. Gas flow rate ratios of BCl_3, CH_4, and N_2 were regulated in the range of 0.4–0.8, 0.3–1.0, and 0.5–1.0 sccm, respectively. The deposition pressure was maintained at 1.0 Torr. A (100)-oriented Si wafer and a quartz wafer were used as a substrate. The deposition time was 30 min for depositing BCN films as thick as 150–300 nm.

The BCN films with various oxygen composition ratios were obtained by controlling the deposition rate. Oxygen atoms are unintentionally incorporated because the base pressure of the quartz reactor is as high as 1×10^{-3} Torr. Oxygen composition ratios increase with a decrease in the deposition rate. In this study, oxide composition ratios from 6% to 15% were used. In wet processes, an acidic solution of oxalic acid and DHF(diluted hydrofluoric acid) are used for post-CMP cleaning and polymer remover after dry etching. NH_4OH and tetramethylammonium hydroxide (TMAH) are used as an alkaline solution for removing resist and polymer. We investigated the influence of those chemicals on BCN films.

A 0.5×0.5 cm^2 sample was immersed into the solutions (0.1 L) using a plastic beaker. The beaker was submerged in a water bath to control the solvent temperature. After the immersion, the wafers were then rinsed with demonized water and dried with N_2 gas. The etching ratio and refractive index measurements were performed by ellipsometry (Focus Ellipsometer FE-III, Rudolph Technologies, Inc.). Fourier transform infrared absorption (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements examined the atomic bonds and the composition ratio of the constituent atoms of the BCN film, respectively. XPS spectra were repeatedly measured after each in-situ Ar ion etching for 30 s to exclude the surface property of the oxidized BCN film. XPS signals from B1s, N1s, C1s, and O1s core levels were detected, and the composition of the BCN film was determined using the XPS signal intensities.

In the wet process, an acid solution of oxalic acid and diluted hydrofluoric acid (DHF) was used for post-CMP cleaning and polymer removal after dry etching [6]. An alkaline solution of NH_4OH and tetramethyl ammonium hydroxide (TMAH) is

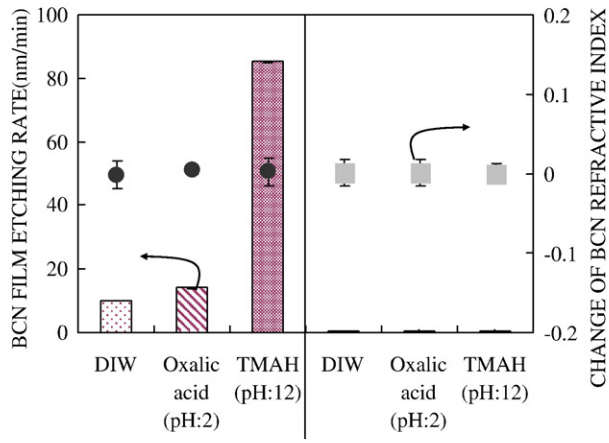

Fig. 2. Etching rate and the change of the refractive index by DIW, oxalic acid (pH2) and TMAH (pH12) for BCN films with more than 10% oxygen (left) and less than 10% oxygen (right), respectively.

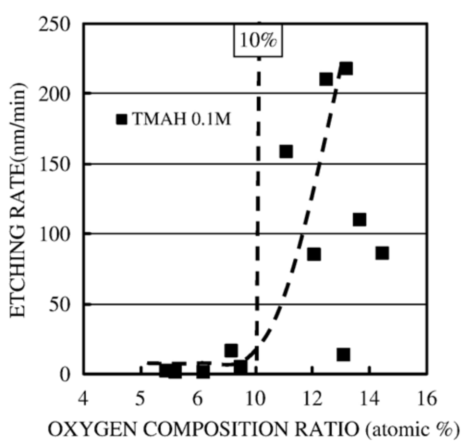

Fig. 1. Etching rate of BCN film of TMAH 0.1 M at RT is plotted as a function of oxygen composition ratio of BCN film.

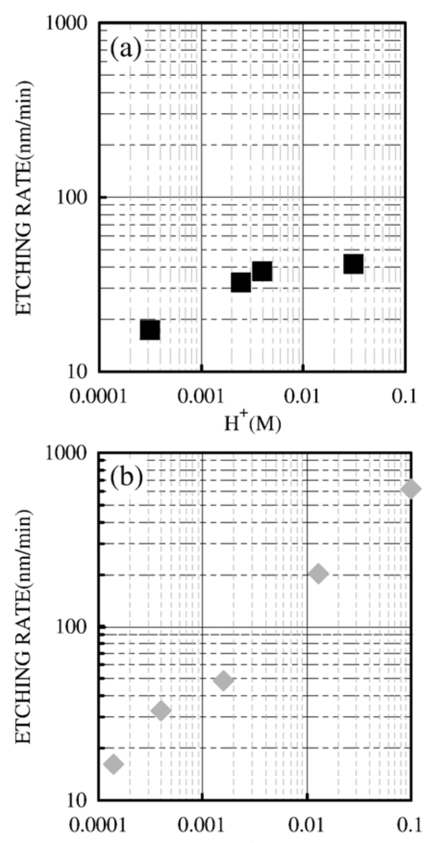

Fig. 3. Dependence of etching rate for BCN film with more than 10% oxygen on (a) H^+ concentration and (b) OH^- concentration.