Diamond & Related Materials 20 (2011) 609–612

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Influence of oxygen plasma treatment on properties of Methyl-BCN film☆

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ARTICLE INFO

Available online 12 January 2011

Keywords:
Methyl
Low-k
Ashing
BCN

ABSTRACT

Methyl-BCN film as a low dielectric material has been investigated by our group for Cu/low-k interconnection. We studied the ashing characteristics of Methyl-BCN films using oxygen plasma. As a contrast, porous-SiOCH films were also treated by oxygen plasma with the same conditions. The change of composition ratio of Methyl-BCN film is less than that of porous-SiOCH film after oxygen plasma treatment. There is no evident change in each bond of Methyl-BCN film after treatment, either. FT-IR analysis was carried out to investigate the chemical bonds of Methyl-BCN films and porous-SiOCH films with and without oxygen plasma treatment. The methyl groups of Methyl-BCN film were more stable than that of porous-SiOCH film.

1. Introduction

In recent years, the large scale integrated circuits which are used in electronic equipments have been made faster in processing speed and more integrated. In order to scale down the ICs, multilayer interconnect technology has been investigated. The conventional interconnect technology which is based on aluminum and SiO_2 has been pushed to its limits because of its remarkable RC delay as the critical dimension of integrated circuits is shrunk [1].

In order to resolve the issue of RC delay due to parasitic capacitance, low resistivity material, such as copper has been used for wiring instead of aluminum. Using low dielectric constant (low-k) material as an interlayer in interconnects is also an effective means of achieving high performance ICs with low RC delay [2,3].

A variety of low-k materials have been investigated for interconnection of next generation LSI. Particular, porous-SiOCH film with a dielectric constant of approximately 2.5 has been studied for many years. However, most porous low-k materials have serious disadvantages such as low mechanical strength and low thermal conductivity. On the other hand, boron carbon nitride film containing methyl groups (Methyl-BCN film) is a promising candidate as one of many low-k dielectrics. We also reported that the hardness and the dielectric constant of Mehtyl-BCN film were 26 GPa and 1.8, respectively [4]. The control of C–H bonds of CH_3 groups is important to achieve low dielectric constant.

Moreover, photoresist stripping is an indispensable step of damascene structure formation for Cu/low-k interconnection and oxygen plasma is commonly used for dry ashing process. The properties of conventional BCN films (which are deposited using BCl_3, CH_4 and N_2 gases) with oxygen plasma treatment have also been investigated [5]. It is also very important for us to study the properties of Methyl-BCN films with oxygen plasma treatment.

In this work, we studied the influence of oxygen plasma treatment on properties of Methyl-BCN films.

2. Experimental

The Methyl-BCN films were deposited by plasma assisted chemical vapor deposition (PACVD) at 350 °C. The substrates which were used in this work were p-type single crystal wafers with (100) orientation. As the source gases, N_2 and TMAB (Tris-di-Methyl-Amino-Boron) gas were introduced into the chamber for deposition. We had studied the chemical and physical properties of TMAB in previous study [6]. And Fig. 1 shows the structural formula of TMAB. The thickness of the Methyl-BCN films was about 200 nm.

To study the properties of Methyl-BCN films with oxygen plasma treatment, dry ashing process was carried out using inductively coupled plasma (ICP) equipment. The samples were situated on the sample holder in the chamber. The chamber of ICP equipment was evacuated up to a base pressure of 2×10^{-2} Pa. During the treatment, the bias power and ICP power were 100 W and 400 W, respectively, with a fixed gas flow rate of 20 sccm. The oxygen plasma treatment pressure was kept at 5 Pa. As a contrast, porous-SiOCH films were also treated with the same conditions.

The chemical bonds of the Methyl-BCN films and porous-SiOCH films before and after oxygen plasma treatments were analyzed by Fourier transformed infrared absorption (FT-IR). In addition, the films were also characterized by X-ray photoelectron spectroscopy (XPS) to investigate the change of each element concentration, and the core level peaks were fitted with a Gaussian distribution.

☆ Presented at NDNC 2010, the 4th International Conference on New Diamond and Nano Carbons, Suzhou, China.

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0925-9635/$ – see front matter
doi:10.1016/j.diamond.2011.01.005

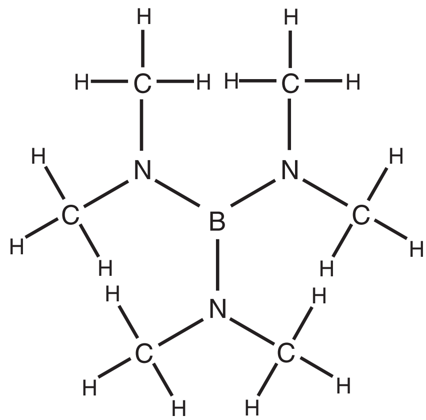

Fig. 1. Chemical structure of tris-di-methyl-amino-boron(TMAB).

3. Results and discussion

Fig. 2 shows the relative changes of the atomic composition ratio before and after oxygen plasma treatment for Methyl-BCN and porous-SiOCH films. The vertical axis is defined as $(\{A_{after} - A_{before}\}/A_{before}) * 100\%$. Here, A_{before} and A_{after} define the atomic concentration of each element of the samples before and after plasma treatment, respectively. After oxygen plasma treatment, the composition ratio of O increased and the C atomic concentration decreased drastically in porous-SiOCH film. It is considered that the increase in composition ratio of O resulted from the chemical reaction between oxygen plasma and porous-SiOCH and generated a 'SiO_2-like layer' [7]. And the C atoms may combine with O atoms and form CO_2/CO, resulting in a decrease of C. However, compared with the porous-SiOCH films, the atomic concentration of each element of Methyl-BCN films changed very little. The reason why the Methyl-BCN films are more stable than the porous-SiOCH films will be discussed in detail later.

Fig. 3(a) shows B 1 s XPS spectra for the Methyl-BCN films with and without oxygen plasma treatment. The B 1 s spectrum is deconvoluted into three components centered at 189.6 eV, 191.1 eV and 192.3 eV attributed to B–C, B–N and B–O, respectively. The spectra illustrates that the intensity of B–O bond increased after oxygen plasma treatments whereas a small amount of decrease in signal intensity of B–C and B–N was found as shown in the figure. The binding energies of B–C and B–N bonds are 448 kJ/mol and 389 kJ/mol, respectively [8]. They were probably broken by oxygen ion during the plasma treatment. Comparatively stable B–O bonds with a binding energy of 808.8 kJ/mol were formed, instead. As shown in Fig. 3(b) and (c), the component at 287.7 eV corresponding to C–N from the C 1 s core level of the Methyl-BCN film and the component at 398.3 eV corresponding to N–C from the N 1 s core level of Methyl-BCN film increased, respectively, after oxygen plasma treatment. It also revealed that the signal intensity of C–O (289.5 eV) and C–C (285.3 eV) increased as well from the C 1 s core level. The signal intensity of C–B decreases slightly as shown in Fig. 3(b). In the N 1 s spectrum, the oxygen plasma treatment resulted in a slight increase in the signal intensity of N–O and a decrease in the N–B component, respectively. From the spectrum of each component, the changes in the signal intensities were not very significant after oxygen plasma treatment.

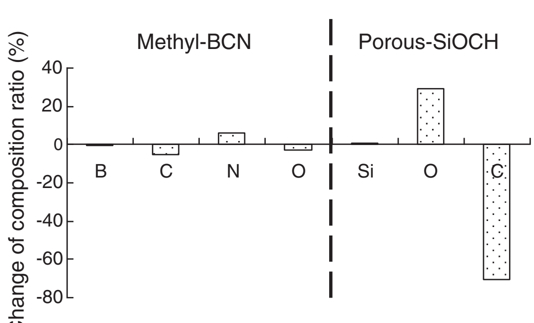

Fig. 2. Change in composition ratio of Methyl-BCN and porous-SiOCH film after 2-min oxygen plasma treatment.

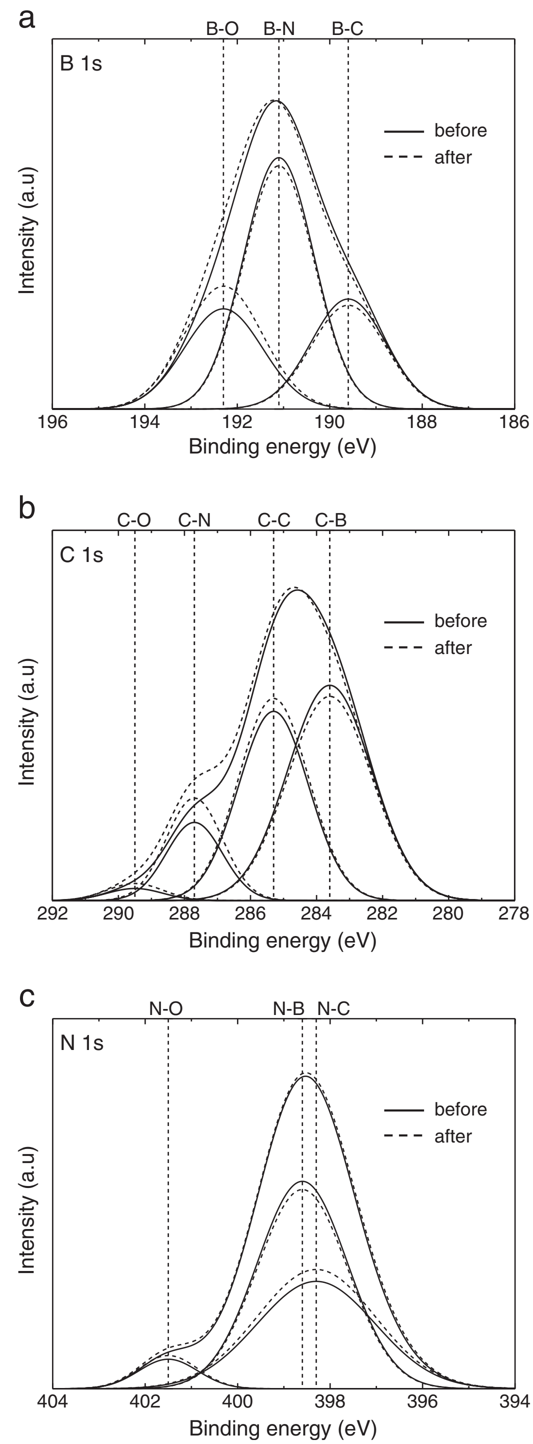

Fig. 3. XPS spectra of the Methyl-BCN films before and after 2-min oxygen plasma treatment.

Fig. 4(a) and (b) show the changes in the signal intensities of C–H bond and Si–CH_3 bond of porous-SiOCH film, respectively, which were