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Synthesis of methyl boron nitride film as low-*k* insulating film for LSI interconnection

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ABSTRACT

Low dielectric constant (k) materials for the ULSI interconnect insulator are required to meet the fast development of high-speed devices. We have investigated low-*k* material of boron nitride containing methyl (methyl boron nitride) by using tris-di-methyl-amino-boron (TMAB) gas. The dielectric constant (k) of the film decreases with decreasing RF plasma power and the k value of the methyl BN film can be achieved as low as 1.8 at 10 W RF plasma power.

Absorption band of the film was observed at 2960 cm^{-1} due to unsymmetrical stretching mode of C–H in CH_3. It is thought that increasing C–H bond with low polarizability and reducing C═N bond with high polarizability can realize a lower k value. The film has also high resistivity of more than 1×10^9 Ω cm and sufficient Young modulus of more than 26 GPa for the interlayer of LSI interconnection. There is a possibility that the dielectric constant can be decreased keeping the BN structure with high strength. The methyl BN film is an extremely attractive material as low-*k* material of next generation devices.

1. Introduction

Low dielectric constant (k) materials for the LSI interconnect insulator are required to meet the fast development of high-speed devices. Devices have been shrunk and processes have become more complex. It is found that hundreds to billions of transistors are assembled on a single chip, resulting in the increase in signal transmission time (i.e., RC delay), power consumption, and wire cross-talk between multilevel interconnects that in turn curtail the benefits of interconnection scaling. In order to achieve high performance interconnection with small RC delay, the integration of a low dielectric constant interlayer (low-*k*) and Cu interconnection is necessary for the next-generation system LSI devices.

Recently, a SiO based porous methyl material such as porous SiOC as low-*k* film has been investigated for next generation system LSI devices [1,2]. However, hardness and modulus of a porous low-*k* film in Cu/low-*k* interconnection are two of the serious issues. Developing a new low-*k* material is important for a stable integration with multi level interconnections.

On the other hand, boron nitride (BN) and boron carbon nitride (BCN) are well-known as a hard material. Young modulus of the BCN has more than 20 GPa [3]. Thus, the BN and BCN are used in a variety of mechanical applications such as edged tools, recent attention has been paid to hexagonal BN (h-BN) because of its superior electronic properties, including a wide bandgap, negative electron affinity, and high electrical resistivity [4,5]. We have investigated device applications of h-BN films deposited by remote plasma-assisted chemical-vapor deposition (PACVD) [6]. We have achieved a dielectric constant as low as 1.9 for boron carbon nitride film without any pores [7].

However, we found serious issues in h-BCN films deposited by PACVD, such as cracking and peeling off the substrates. Adding carbon atoms into BN films is effective in resolving these issues. No physical change occurs for boron carbon nitride (BCN) films with a C composition ratio >18%, even after undergoing a wet process with deionized water [8,9]. The dielectric constant of low-*k* film increases by trapping water in the pores, the corrosion of Cu wiring is induced by water residue in the film, and the interconnection reliability as a whole is degraded. However, increasing the carbon-composition ratio in the BCN film can suppress incorporation of water into the film [10]. Nonetheless, the *k*-value of BCN film deposition when using BCl_3 gas is unstable. We attempted more stable BCN film deposition by using tris-di-methyl-amino boron (TMAB) gas with a methyl group and without chlorine [11]. It is reasonable to consider that formation of methyl-base into the amorphous region of the BN film may lead to a reduction in the dielectric constant due to an introduction of nanopores. Such a BN film is designated as methyl boron nitride here.

In this study, we investigated methyl boron nitride film with high mechanical strength. This paper reports on the film property dependence of boron nitride film containing a methyl group, using TMAB gas with RF plasma power.

2. Experimental procedure

Fig. 1 shows a deposition chamber of horizontal furnace type. In this experiment, the TMAB gas was heated at 100 °C to obtain

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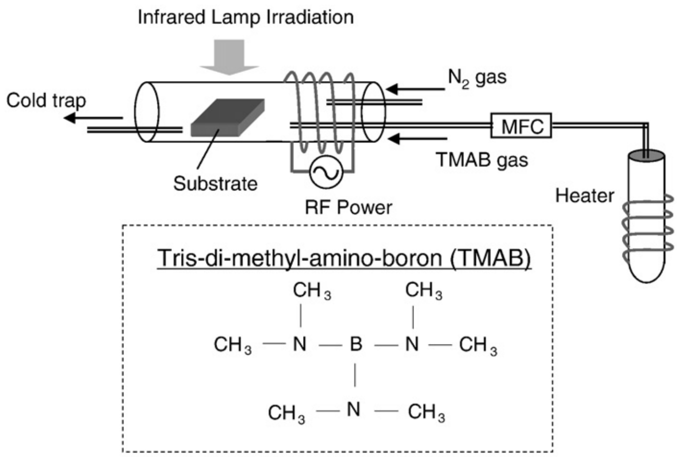

Fig. 1. Deposition chamber and chemical structure of tris-di-methyl-amino-boron (TMAB).

sufficient vapor pressure (180 Torr). At first, we tried thermal deposition process for methyl BN film deposition. TMAB gas and N_2 gas were introduced into the quartz reactor. A coil was installed around the quartz reactor, and radio-frequency (RF) power of 80 W was supplied to the coil to produce N_2 plasma remotely by induction coupling. Even if 730 °C, the methyl BN film was not deposited. Therefore, TMAB gas cannot be decomposed by thermal process. On the other hand, TMAB can be easily decomposed by plasma. Methyl BN films were deposited by remote plasma chemical vapor deposition using TMAB gas at 350 °C. Fig. 1 also represents the chemical structure of tris-di-methyl-amino-boron (TMAB: $B[N(CH_3)_2]_3$) gas. In the TMAB structure, B atom of the center has three N atoms, and each N atom has two CH_3. The properties of BCN film by using BCl_3 gas were reported [6]. Substrates were placed on the holder inside the reactor tube for deposition. N_2 gas flow rate and TMAB gas flow rate were 5 sccm and 0.5 sccm, respectively. The deposition temperature was 350 °C. RF plasma power was controlled from 10 W to 90 W. The films with the thickness of nearly 200 nm–300 nm were deposited on the Si substrate.

In evaluation, we analyzed the film bonding by Fourier transform infrared absorption (FTIR) spectrum. X-ray photoelectron spectroscopy (XPS) measurements were mainly carried out to examine the atomic bonds and the composition ratio of the constituent atoms of the film.

Sample with a step of the film by partly masking during the deposition was prepared. The film thickness was measured by using alpha-step. Curent–voltage (*I*–*V*) and capacitance–voltage (*C*–*V*) characteristics were measured by using a metal–insulator–semiconductor (MIS) structure of Au/methyl BN/Si at room temperature. The dielectric constant was estimated from the capacitance in the accumulation region of the Au/methyl BN/p-Si sample and the film thickness. The dielectric constant of the films was calculated from the capacitance–voltage (*C*–*V*) measurement at 1 MHz at the accumulation region.

The strength (Young modulus) of the films can be measured by a nano-indentation method [12]. The nano-indentation method has been widely used to evaluate Young modulus of thin low-*k* films for

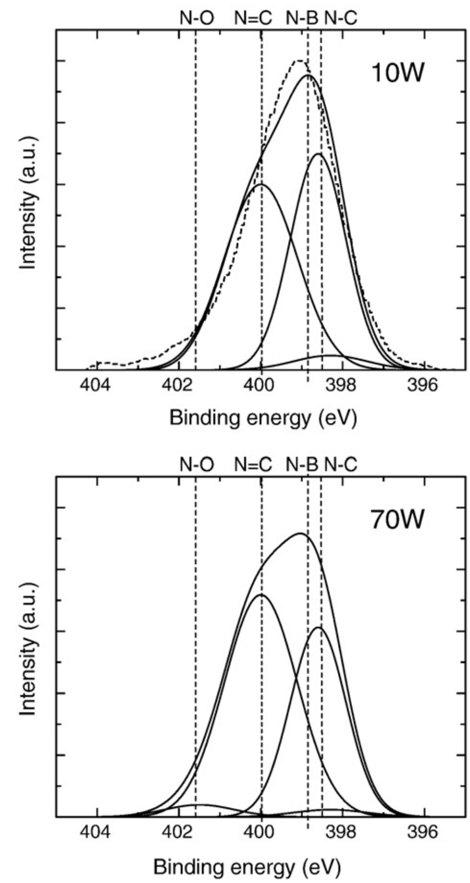

Fig. 3. XPS spectra of methyl BN film for RF plasma power (10 W and 70 W).

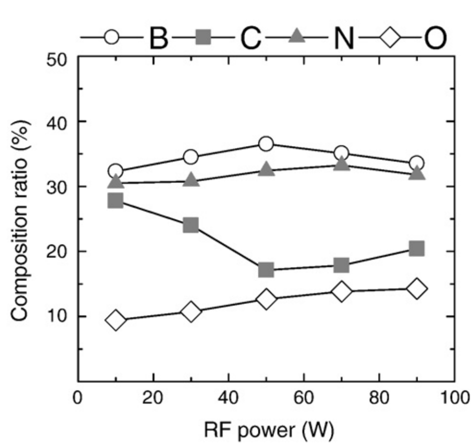

Fig. 2. Compositions of B, N, C and O atoms in the film plotted as a function of the RF plasma power.

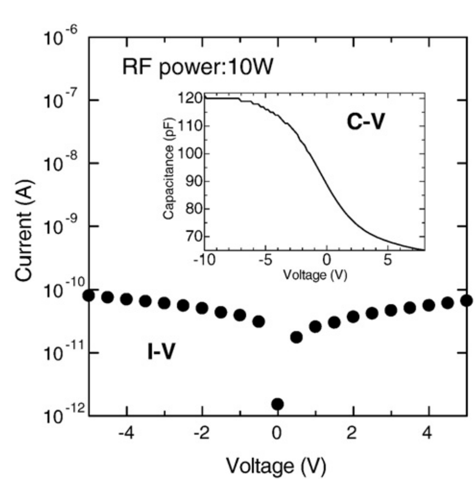

Fig. 4. Current–voltage (*I*–*V*) and capacitance–voltage (*C*–*V*) characteristics of methyl-BN film deposited by RF power 10 W.