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Influence of moisture on BCN (low-*K*) film for interconnection reliability

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Abstract

The integration of low dielectric constant (low-*K*) interlayers and Cu wiring is necessary to produce next-generation LSI devices. Low-*K* films of porous type have been investigated to reduce a dielectric constant (*K* value). However, most porous low-*K* materials have faced a serious problem of water incorporation during the wet processes used in making the interconnections. Thus, the influence of moisture on boron carbon nitride (BCN) films is important to investigate. To study water-treated BCN films, we measured the current-versus-voltage (I–V) and capacitance-versus-voltage (C–V) characteristics of BCN films, using an MIS (mercury electrode/BCN/Si substrate) structure. We found that both the leakage current and dielectric constant of BCN films decrease as the film's carbon-composition ratio increases. D_2O detection using thermal desorption spectroscopy (TDS) reveals that BCN films with carbon-composition ratios greater than 30% can suppress the incorporation of water into the film. Desorption of hygroscopic water from the BCN film occurred at temperatures as low as 390 °C, which is a normal LSI-production process temperature. The use of BCN film appears to resolve the serious problem of water incorporation into the porous low-*K* materials. In addition, we have investigated a conduction mechanism resulting from the water protons, based on the frequency dependence of the BCN film impedance before and after water treatment.

Keywords: Dielectric constant; Low-*K*; BCN; Moisture; Water; TDS; Cu

1. Introduction

Interconnection design rules keep moving toward reducing the die size. As a result, devices have shrunk, processes have become more complex and new materials, such as porous dielectrics, have been introduced. To achieve high performance interconnection with small RC delay, the integration of a low dielectric constant (low-*K*) interlayer and Cu wiring is necessary in the next-generation LSI devices. Recent efforts have focused on the development of new low-*K* materials with a dielectric constant lower than two [1,2]. Although some porous low-*K* films reduce the *K* value, we have achieved a dielectric constant as low as 1.9 for the BCN films without pores [3].

In contrast to cubic boron nitride (c-BN), known as a hard material, and used in a variety of mechanical applications, 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 [4–7]. It is possible to use h-BN in electronic and optoelectronic devices. We have investigated device applications of h-BN films deposited by remote plasma-assisted chemical-vapor deposition (PACVD) [5] but found serious issues such as the PACVD deposited h-BCN films cracking and peeling off the substrates. Adding carbon atoms into BN films is effective in resolving these issues [8]. No physical change occurs for boron carbon nitride (BCN) films with a C composition ratio larger than 18%, even after undergoing a wet process with deionized water. Therefore, BCN films show promise for electronic devices.

Because wet processes, such as polymer removal, CMP and electrochemical plating are required in the interconnection process shown in Fig. 1, porous low-*K* films have to deal with this moisture [9]. Thus, it is important to investigate the influence of moisture on BCN films.

In this paper, we report that the influence of water on BCN films decreases as their carbon-composition ratio increases. We also found that desorption of hygroscopic water from BCN films occurs at temperatures as low as 390 °C, which is a normal process temperature for LSI production. The introduction of BCN films, therefore, could resolve the problem of water incorporation into porous low-*K* materials.

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2. Experimental procedure

BCN films were deposited by plasma-assisted chemical-vapor deposition (PACVD) at 390 °C [2]. The substrate, a (100)-oriented Si wafer or a quartz wafer, was set and source gases, boron trichloride (BCl_3), methane (CH_4), and nitrogen (N_2), 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. BCl_3 was transported with hydrogen (H_2) gas near the substrate. CH_4 was added to the N_2 plasma. The substrate temperature was kept at 390 °C by an external furnace. The gas-flow rates of BCl_3, CH_4, and N_2 were regulated in the range of 0.4 to 0.8 sccm, 0.3 to 1.0 sccm, and 0.5 to 1.0 sccm, respectively. The deposition pressure was kept at 1.0 Torr and the deposition time was 30 min. BCN films with thicknesses ranging from 150 to 250 nm were deposited in this experiment.

The carbon-composition ratio in the BCN films is controlled by the CH_4 gas flow ratio. This study used the BCN films with carbon compositions of 12.6% to 35.7%. Physical change such as color, adhesion or thickness didn't occur in the BCN films with a carbon-composition ratio larger than 18%, even after wet treatment with deionized water (DIW).

The properties of the BCN films were measured by thermal desorption spectroscopy (TDS), Fourier transform infrared absorption (FTIR), and X-ray photoelectron spectroscopy (XPS). TDS measurements were performed to confirm the existence of hygroscopic water in the BCN films. Deuterium (D) was used to distinguish the influence of water treatment from the hydrogen atoms incorporated in the deposited BCN films [10]. The TDS spectrum was measured at a rate of 1 °C/sec in the range of 60 to 1000 °C on a BCN film treated with D_2O (M/z=20) ambient for 60 hours. FTIR and XPS measurements were performed to examine the atomic bonds and the composition ratio of the constituent atoms of the BCN films, respectively.

The current-versus-voltage (I–V) and capacitance-versus-voltage (C–V) characteristics of the BCN films were measured using a metal electrode/insulator/semiconductor (MIS) structure. In particular, a mercury electrode was used to analyze the water-treated films. For Au electrode deposition by PVD, any water in the BCN films is evaporated because of the vacuum. On the other hand, using a mercury probe allowed measurement of the I–V and C–V characteristics of the BCN films without evaporating the water in the films.

Impedance-versus-frequency (Z–f) characteristics of the BCN films were investigated using another structure, with long distance pass, to study the influence of water incorporated into the BCN film. The Z–f measurement was performed in the frequency range from 100 Hz to 10 K Hz using a dielectric-impedance measurement system. The BCN sample was fabricated using a quartz substrate to measure Z–f characteristics. Prior to depositing the BCN film, an interdigital electrode was formed on the quartz substrate by sputtering Ti followed by photolithography. Ti is used because of better adhesion between the BCN film and the Ti electrode, compared with Al or Au electrodes. The spacing of the interdigital electrode was 150 μm wide and the thickness was 300 nm. BCN films were deposited on the quartz substrate with the Ti electrode. This sample configuration avoids a direct influence of hygroscopic water on the electrode.

3. Results and discussion

The dependence of the FTIR spectrum on the carbon-composition ratio in the BCN films was investigated. All samples have a large absorption band detected at 1380 cm^{-1}, resulting from the stretching mode of B–N in the hexagonal BN [11]. Absorption bands resulting from H–O–H are reported to be at 3440 and 3230 cm^{-1} [12–14]. Fig. 2 shows the dependence of the intensities of H–O–H bands on the carbon-composition ratio of the BCN films exposed to the air for one week after deposition. The vertical axis shows the normalized peak intensities of H–O–H bands of the FTIR spectrum. The peak intensities of the H–O–H bands for the BCN films exposed to the air for one week after deposition are normalized for the peak intensities of H–O–H bands of the as-deposited BCN film. The FTIR peak intensity of H–O–H bands decreases as the carbon-composition ratio in the BCN films

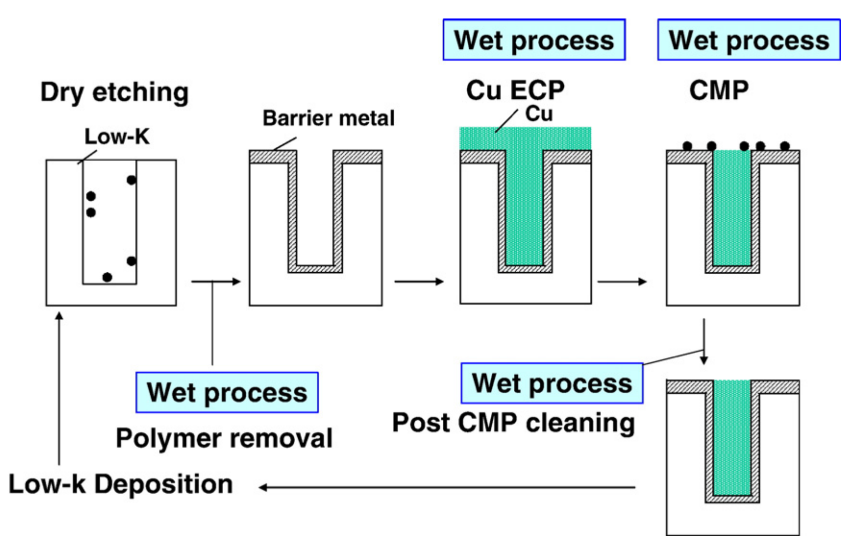

Fig. 1. Cu/Low-*K* interconnection process flow.