Applied Surface Science 255 (2009) 3719–3722

Contents lists available at ScienceDirect

Applied Surface Science

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

Influence of Cu electroplating solutions on boron carbon nitride (BCN) film

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ARTICLE INFO

Article history:
Received 6 August 2008
Received in revised form 6 October 2008
Accepted 7 October 2008
Available online 1 November 2008

Keywords:
BCN
Low-k
Cu
Electroplating
Boron carbon nitride

ABSTRACT

Cu electroplating is required for the fabrication of Cu/low-k interconnections. The permeation of a plating solution into low-k films during Cu electroplating is a serious challenge for 45-nm nodes and more complex devices. We investigated the influence of Cu electroplating solutions on boron carbon nitride (BCN) as a low-k film. After dipping it into a Cu electroplating solution that contained additives, the BCN film's hydrophilic surface changed to a hydrophobic surface, and the incorporation of water into the BCN film was suppressed by surfactant adsorption. Sulfuric residue was detected on the BCN sample by thermal desorption spectroscopy after treatment in the Cu electroplating solution with additives; however, it was found through electrical measurements that this solution did not affect the leakage current or the dielectric constant of the BCN film. We successfully fabricated an electroplating Cu layer on a BCN film with good adhesion, and we believe that this BCN film is a sufficiently useful material for Cu/BCN integration in LSI.

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1. Introduction

To achieve high-performance interconnections for next-generation system LSI devices with small RC delays, the integration of a low-dielectric constant (low-k) interlayer with Cu wiring is necessary. Recent efforts have focused on the development of new low-k materials with a dielectric constant under 2 [1,2]. Although some porous low-k films reduce the *k* value, we have achieved a dielectric constant as low as 1.9 for boron carbon nitride (BCN) [3].

According to the ITRS roadmap, beyond 45-nm nodes, the thickness of the barrier metal layer for Cu diffusion prevention should be less than 5 nm [4]. Thinning the barrier metals and increasing the porosity of low-k films have caused the emergence of a new failure mode in porous low-k films, such as the voiding phenomenon, which could be attributed to the permeation of the plating solution during Cu electroplating, as shown in Fig. 1. A defect-free barrier metal layer achieved by chemical vapor deposition (CVD) with atomic layer deposition was proposed to prevent low-k film voiding. However, the CVD barrier penetrates porous low-k films [5]. In addition, physical vapor deposition (PVD) was unable to eliminate the possibility of pinholes on the barrier. If the Cu^+ ions of an electroplating solution penetrate into the BCN film, the Cu in the low-k film may cause an increase in leakage currents. Even in the presence of an electric field, Cu^+ ions can drift rapidly through low-k films, causing reliability problems.

We previously reported that Cu diffusion into a BCN film by thermal annealing can be suppressed compared with a conventional porous SiOC film [6]. No physical change occurs for BCN films with a carbon composition ratio larger than 20%, even after undergoing a wet process with deionized water (DIW). In particular, wet processes such as polymer removal, chemical mechanical polishing, and electrochemical plating are required in the interconnection processes, and porous low-k films must be able to cope with this moisture [7]. In previous studies, we investigated the influences of water or chemicals on BCN films [8–10]. In addition, the influence of a Cu electroplating solution on porous low-k films has been reported [11]. To achieve reliable interconnection using BCN films, it is important to investigate the penetration of an electroplating solution into BCN films. In this paper, we report the influence of Cu electroplating solutions on the properties of BCN films.

2. Experimental procedure

A range of BCN films were deposited on Si substrates using an inductively coupled plasma-type RF plasma CVD. The RF power was 500 W. The source gases were boron trichloride (BCl_3), methane (CH_4), and nitrogen (N_2). H_2 gas was used as a carrier gas. BCl_3 was transported near the substrate. CH_4 was added to the N2 plasma. The gas-flow rates of BCl_3, CH_4, and N_2 were regulated in

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0169-4332/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.apsusc.2008.10.046

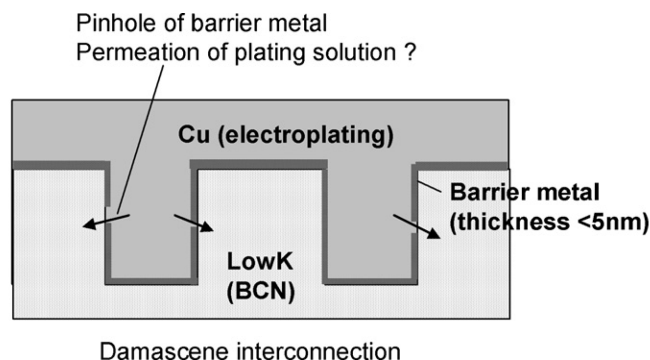

Fig. 1. Pinholes of Cu/low-k damascene structure.

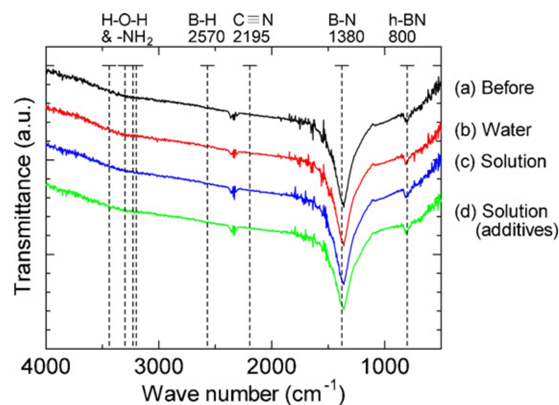

Fig. 2. FTIR spectra of BCN films (a) before treatment (Ref.), (b) after dipping in water (DIW), and (c) after dipping in electroplating solution without and (d) with additives.

the range of 15, 45, and 45 sccm, respectively. The deposition pressure was kept at 0.3 Torr, and the deposition time was 30 min. BCN films with thicknesses ranging from 150 to 250 nm were deposited in this experiment.

Conventional Cu electroplating solutions based on the standard cupric sulfate aqueous solution ($CuSO_4$) were used, together with three additives (suppressor, accelerator, and leveler). BCN films were treated by dipping them in DIW and Cu electroplating solutions with and without (conventional) additives. BCN films were dipped in these solutions for 5 min at 30 °C and rinsed with DIW for 1 min followed by exposure to an air blow. The properties of BCN films after treatment in Cu electroplating solutions were measured by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared absorption (FTIR), and thermal desorption spectroscopy (TDS).

FTIR and XPS measurements were performed to examine the atomic bonds and the composition ratio of the constituent atoms of BCN films, respectively.

TDS measurements were performed to confirm the existence of water (H_2O), sulfur (S), and copper (Cu) in Cu electroplating solutions ($CuSO_4$) within BCN films. The TDS spectrum was measured at a rate of 1 °C/s in the range of 60–1000 °C on a BCN film after dipping the film into DIW and Cu electroplating solutions. The influence of Cu electroplating solutions on the electrical characteristics of BCN films was evaluated by current–voltage (I–V) and capacitance–voltage (C–V) measurements using a metal electrode/insulator/semiconductor (MIS) structure.

3. Results and discussion

Fig. 2 shows the FTIR spectra of BCN films: (a) before treatment (Ref.), (b) after dipping in water (DIW), and (c) after dipping in the electroplating solution without and (d) with additives. All samples show a large absorption band at 1380 cm^{-1} resulting from a stretching of the B–N bonds in the hexagonal BN structure [12]. The FTIR spectrum of BCN films after dipping in Cu electroplating solutions with and without additives was similar to that before treatment. The peak intensity of B–N (1380 cm^{-1}) after dipping in the Cu electroplating solution with additives decreased a little. Absorption bands resulting from H–O–H were observed at 3440 and 3230 cm^{-1} [13]. The FTIR peak intensities of H–O–H due to water were not observed for all samples. Thus, BCN films were not influenced by water moisture from the solutions.

XPS measurements examined the composition ratio of the constituent atoms of BCN films before and after dipping in the Cu electroplating solution with additives. Fig. 3 shows the XPS depth profile of the BCN film after dipping it into the Cu electroplating solution with additives. From the photoelectron signal intensities, the composition ratios of the B(1s), C(1s), and N(1s) atoms were estimated to be 43–46%, 18–21%, and 35–36%, respectively. Changes in signal intensities for the B–C (189.6 eV) and B–N (191.1 eV) bonds in the B1s spectrum and the N–B bonds (398.6 eV) in the N1s spectrum were not observed after dipping in the Cu electroplating solution with additives. Therefore, the bonds of the BCN film were not influenced by the Cu electroplating solution. Changes in physical characteristics such as color, adhesion, or thickness did not occur in BCN films after treatment with water (DIW) and Cu electroplating solutions with and without additives. The extremely small XPS intensities of S(2s) and Cu(2p) could make it difficult to detect S and Cu atoms by this method. We therefore attempted to detect S and Cu using TDS.

By TDS measurements, we examined the incorporation of water ($m/z = 18$), SO ($m/z = 48$), SO_2 ($m/z = 64$), and Cu ($m/z = 63$) into BCN films. TDS analysis has been found to be more sensitive than FTIR analysis. Fig. 4 shows TDS spectra of (a) water ($m/z = 18$), and (b) SO ($m/z = 48$) and Cu ($m/z = 63$) after dipping in water (DIW) and Cu electroplating solution with additives. A TDS spectrum ($m/z = 18$) with a peak at 28 °C was observed for the BCN film after water (DIW) treatment. However, the TDS intensity of water ($m/z = 18$) for the Cu electroplating solution with additives was much smaller than that for water treatment, as shown in Fig. 4(a). It is likely that the incorporation of water was suppressed by a surfactant in the additives. The contact angle for the dropped water

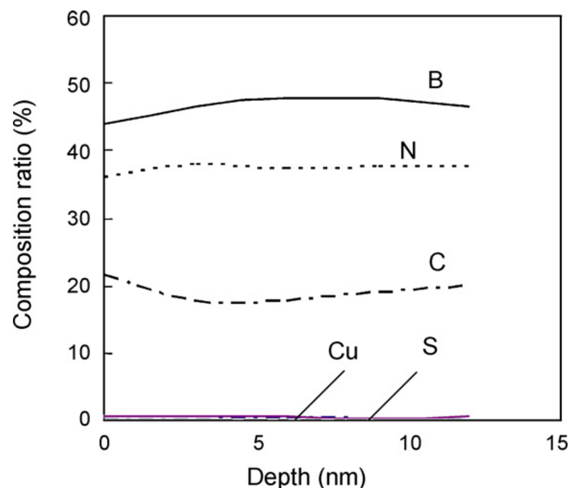

Fig. 3. XPS depth profile of BCN film after treatment in a Cu electroplating solution with additives.

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