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Microelectronic Engineering 82 (2005) 416–421

MICROELECTRONIC ENGINEERING

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Study of plasma mechanisms of hybrid a-SiOC:H low-*k* film deposition from decamethylcyclopentasiloxane and cyclohexene oxide

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Abstract

The deposition of hybrid a-SiOC:H dielectric films from decamethylcyclopentasiloxane/cyclohexene oxide/helium (D5/CHO/He) plasmas has been investigated in various operating conditions. In order to understand the influence of molecule fragmentation on the film formation, the species in the plasma were monitored by optical emission spectroscopy and mass spectroscopy. The films were analyzed with spectroscopic ellipsometry and Fourier transform infrared spectroscopy. The CHO molecule loss rate under fragmentation and film formation was always much higher than that of D5, with the ratio depending on the plasma conditions. The CHO was found to lose at least CO, CH, H and C_3 groups whereas D5 main reactions in plasma occurred through Si–CH_3 and C–H bond dissociation, leaving its cyclic structure unaltered. This suggested that different hydrocarbon fragments got incorporated in the film thanks to the presence of CHO in the gas feed compared to D5 alone deposited films. Moreover some Si–O–Si structure indicated a high level of the D5 cycle preservation in the film. The deposition rate increased linearly with RF plasma power for D5 films and for D5/CHO films. It was enhanced by the presence of CHO in the plasma.

Keywords: PECVD; D5; Porogen; Mass spectroscopy; Fragmentation

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1. Introduction

The increasing interconnection density in microelectronic makes the signal delay and cross

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doi:10.1016/j.mee.2005.07.025

talks between metal lines critical for performances of ultra-large-scale-integrated (ULSI) devices. To limit these detrimental effects, it is necessary to develop dielectric materials that have the lowest dielectric constant "*k*" (relative permittivity). For 300 mm technology and devices manufactured at the 65 nm node and beyond, materials with *k* values lower than 2.5 are expected. Porous amorphous carbon doped oxides (a-SiOC:H) deposited by plasma enhanced chemical vapor deposition (PECVD) are interesting films to address this challenge. A two step porogen approach is one of the routes towards such material. The first step is based on the hybrid, or multiphase deposition. This method consists in admixing an organic precursor (porogen) with an organosilicon precursor (a-SiOC:H matrix) during the deposition. The porogen yields a thermally unstable CH_x phase that is removed during a specific curing (for example: thermal annealing) [1]. Following this approach, films with *k* as low as 2.2 have been reported on lab scale [2] from plasma enhanced chemical vapor deposition (PECVD) of decamethylcyclopentasiloxane (D5; $Si_5O_5C_{10}H_{30}$) as a-SiOC:H matrix and cyclohexene oxide (CHO; $C_6H_{10}O$) as porogen. The cyclic siloxane molecules are interesting because it is expected that the preservation of the cyclosiloxane structure would lead to lower density of the material and then lower dielectric constant. Moreover, no oxidant gas is added, in order to prevent a possible alkyl group oxidation, hence guarantee a high CH_x incorporation in the film.

In order to understand the influence of molecule transformation on film properties, the plasma was monitored by optical emission spectroscopy and the gas phase was analyzed by mass spectroscopy. A correlation was established between these data and the film properties for various conditions.

2. Experimental details

The deposition reactor was a 200 mm commercial PECVD chamber, with a RF 13.56 MHz capacitive coupling power source on a heated ($T = 180$ °C) and electrically grounded susceptor. Liquid precursors (D5 and CHO) were mixed with helium and vaporized. They were homogeneously distributed in the chamber through the showerhead, also used as top electrode. The films were deposited on Si substrates and some of the deposition parameters were changed during the experiments: applied RF power (RF = 100–600 W), reactor pressure ($P = 1$, 3, 5 Torr), gas mixture (He/D5 or hybrid (He/D5/CHO).

The plasma was monitored by an AVASPEC 2048 optical emission spectrometer (400–820 nm, resolution: 0.3 nm) in order to assess the emitting radicals or molecules in the plasma.

Neutral molecules, ions or radicals with a mass to charge ratio (m/z) up to 300 amu (arbitrary mass units) were analyzed by a SMART IQ+ Quadrupole Mass Spectrometer.

The film thickness and refractive index were measured by spectroscopic ellipsometry (Kla-Tencor). The deposition rate corresponds to the ratio of film thickness by the deposition time.

The chemical structure of the material was identified on a BIORAD QS-500 Fourier transform infrared spectrometer (FTIR; 400–4000 cm^{-1}). All FTIR spectra were normalized with respect to thickness and baseline corrected for a better comparison.

3. Plasma and gas phase analysis

Fig. 1 shows the mass spectra of precursor and hybrid deposition plasma. The similarities among these spectra indicate that the parent molecules are the main gaseous species. There are no major reactions between D5 and CHO in the plasma since the hybrid plasma spectrum has the same peaks as CHO and D5 ones [3]. This confirms that gas phase reactions main mechanism is fragmentation, when electrons and metastable species collide with precursor and porogen molecules. The D5/helium plasma spectrum (not represented) is very similar to D5 spectrum obtained without plasma. Nevertheless a slight uptake is seen for $m/z = 15$, caused by CH_3 radicals from Si–CH_3 bonding cleavage in D5. Concerning CHO dissociation, the two peaks $m/z = 26$ and 28 in hybrid spectrum, absent of D5 alone spectrum, can be attributed to C_2H_2, or C_2H_4/CO/Si, respectively. They indeed reveal the porogen carbon chain fragmentation,