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The dielectric response of low-k interlayer dielectric material characterized by electron energy loss spectroscopy

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ABSTRACT

In this study, the dielectric response of low-k dielectric materials has been characterized by electron energy loss spectroscopy. A widely accepted fast Fourier transform based Kramers–Kronig method (Johnson, 1975) [3] has been used to derive the high-frequency response of these materials. We used three different low-k dielectric materials to find out the effect of porosity and carbon content on the dielectric response of materials. Amorphous SiO_2 and SiC:H samples are used for comparison. All samples were deposited by plasma-enhanced chemical vapor deposition technique. A Lorentzian-based oscillator model has been used to determine the eigen-energy of excitations by fitting the measured loss function. The model is specially designed to let all oscillator parameters move freely and find their most probable position by using a least square fitting analysis procedure. The band gap for amorphous SiO_2 which corresponds to the first absorption peak in the imaginary part of dielectric function is found to be at around 9 eV. We observed that in the case of dense low-k material, there appears a finite density of states (DOS) inside the band gap of SiO_2, whereas the inclusion of porosity into dense low-k network diminishes the in-gap DOS and widens the band gap to around 10 eV.

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1. Introduction

Continuous improvements in device integration and performance have been achieved through feature size reduction and the scaling down of device dimensions to the deep sub-micrometer level. The coupling effect of the inter-metal capacitance with line resistivity has become a limiting factor for ultra-large-scale integration of electric circuits. To reduce this problem, low dielectric constant (low-k) materials are required for use as inter-layer dielectric and low resistivity conductors as metal lines. Thus, much research effort has been devoted to develop new low-k dielectric materials to replace the conventional silicon dioxide ($k = 3.9–4.3$) [1] dielectrics. Carbon-doped silicon oxide (SiCOH) films have gained much attraction from both academia and microelectronic industry because of their low dielectric constant as well as their good mechanical strength and high thermal stability. Furthermore, porosity has been introduced to further lower the k-value on the cost of mechanical strength [2]. While these materials are already widely employed in the manufacturing of complex logic devices, the origin of their properties are not yet well understood. This lack of insight makes it difficult to improve the material properties in an effective, knowledge based manner.

In this paper transmission electron microscopy (TEM) in combination with electron energy loss spectroscopy (EELS) is used to study the dielectric response of these low-k materials. However, there are two problems to overcome for the low-k film analysis by TEM/EELS technique. One is that the low mechanical strength of these low-k materials needs special handling during sample preparation by the conventional method: mechanical polishing followed by ion milling process. Other one is the prevention of damage by high-energy incident electron beam in TEM. The film stability is a major concern for the TEM/EELS investigation. Local heating of the film may occur during TEM observation especially in samples with low thermal conductivity. As a matter of fact, we have encountered shrinkage of the low-k film as an indication of the damage during TEM measurements.

In this study we have examined the influence of porosity and carbon content on the dielectric response of such low-k dielectric materials. The investigations were performed on EELS low-loss spectrum and implementing a well-established Kramers–Kronig program [3] to determine the effective dielectric properties of the materials. The eigen-energy and corresponding transition

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probability have been calculated by comparing a Lorentzian-based oscillator model with the loss-function. For better accuracy in model parameters, the fitting procedure needs to be performed on the loss-function and dielectric function altogether.

2. Experimental

EELS experiments were performed with a TEM Philips CM20 FEG operated at 200 kV. Low-k dielectric samples used for this study are listed in Table 1. The dielectric constants of these low-k materials are smaller than those of SiO_2 because of the replacement of oxygen by methyl group, where Si—CH_3 bond polarizability is lower than the Si—O bond polarizability. The porosity has been introduced into the network by first depositing a sacrificial chemical called porogen and removing it afterwards by annealing. The sample preparations for TEM have been done by the classical approach i.e. mechanical polishing followed by ion milling process. The dielectric constants electrically measured by Hg probe method are listed in Table 1 for low-k dielectric samples used in this study. Plasma-enhanced chemical vapor deposition (PECVD) technique is used to deposit amorphous SiO_2 and SiC:H (hydrogenated silicon carbide) materials with dielectric constants of 3.9 and 2.9 respectively and are used for the comparison. The atomic concentration of elements present in the material has been determined by both energy dispersive X-ray spectroscopy (EDX) and EELS measurements. Low-loss EELS spectra were then processed by a fast Fourier transform (FFT)-based Kramers–Kronig analysis technique[3]. The energy resolution, measured at full width at half maximum (FHWM) of the zero-loss peak (ZLP) in the EELS low-loss spectrum was found to be 1.1 eV. In order to determine the inter-band transition energies, a Lorentzian-based oscillator model was used. The program was specially designed to obtain the transition energies by a least square method. Simultaneously we fitted the experimental loss-function and both real and imaginary parts of the dielectric function to get a better accuracy in eigen-energies.

The observed low-loss EELS spectrum is connected to the imaginary part of reciprocal dielectric function $\mathrm{Im}(-1/\varepsilon(E))$ called the energy-loss function as [4]:

$$S(E) = \frac{I_0 t}{\pi a_0 m_0 v^2} \mathrm{Im}\left[-\frac{1}{\varepsilon(E)}\right] \ln\left[1 + \left(\frac{\beta}{\theta_E}\right)^2\right], \quad (1)$$

where $S(E)$ represents single scattering distribution, I_0 – zero-loss intensity, t – specimen thickness, β – collection semi-angle, $\theta(E)$ – scattering angle, $\varepsilon(E)$ – complex dielectric function, α_0 – Bohr radius, m_0 – electron rest mass and v is electron velocity.

After finding the $\mathrm{Im}(-1/\varepsilon)$ from Eq. (1), FFT-based Kramers–Kronig relation has been used to obtain $\mathrm{Re}(1/\varepsilon)$ that leads to the determination of dielectric permittivity ε_1 and energy dissipation ε_2 [4] as:

$$\varepsilon_1(E) = \frac{\mathrm{Re}\left(\frac{1}{\varepsilon(E)}\right)}{\left\{\mathrm{Re}\left(\frac{1}{\varepsilon(E)}\right)\right\}^2 + \left\{\mathrm{Im}\left(\frac{-1}{\varepsilon(E)}\right)\right\}^2},$$

$$\varepsilon_2(E) = \frac{\mathrm{Im}\left(\frac{1}{\varepsilon(E)}\right)}{\left\{\mathrm{Re}\left(\frac{1}{\varepsilon(E)}\right)\right\}^2 + \left\{\mathrm{Im}\left(\frac{-1}{\varepsilon(E)}\right)\right\}^2}.$$

These experimentally derived dielectric functions are then used to be fitted by a Lorentzian oscillator model [5]. The eigen-energies for oscillators were calculated from the least square fitting procedure in Lorentz oscillator model in which real part $\varepsilon_1(E)$ and imaginary part $\varepsilon_2(E)$ of the dielectric function are given by:

$$\varepsilon_1(E) = 1 + E_p^2 \sum_{i=1}^{n} \frac{f_i(E_i^2 - E^2)}{(E_i^2 - E^2)^2 + g_i^2 E^2}, \quad \varepsilon_2(E) = E_p^2 \sum_{i=1}^{n} \frac{f_i g_i E}{(E_i^2 - E^2)^2 + g_i^2 E^2}, \quad (2)$$

where E_p, E_i, f_i and g_i are the plasmon energy, eigen-energy, oscillator strength, and damping factor respectively, and n represents the number of oscillators used for the fitting. The damping factor is related to the distribution of energy levels around the eigen-energy E_i – sharper absorption lines correspond to the smaller values of g_i, arising from regions of parallel energy bands. The oscillator strength f_i carries information about number of states contributing to the resonance at eigen-energy E_i.

The measured loss-function has been expressed as the sum of a set of oscillators vibrating at their respective resonance energies. The values of E_i, f_i and g_i were derived from Eq. (2), following the least square fitting procedure.

3. Theoretical

To model the impact of chemical composition and porosity on the dielectric properties of low-k oxides, we employ the same atomistic model of organosilicate glasses used in previous studies of their elastic properties [6]. This model is based on an amorphous unit cell of 64 Si atoms, free of coordination defects. The Si atoms are interconnected by random distributions of O and CH_2 bridges, according to the desired C and O content. Porosity is modeled by removing groups of Si atoms and their connecting groups, saturating the resulting dangling bonds at the pore surface by CH_3 groups. The resulting structures are of slightly distorted cubic shape, depending on the composition. The side lengths of unit cell are between 1.45 ± 0.1 nm for SiO_2 and 1.5 ± 0.1 nm for $Si(CH_2)_2$ and, the angles between lattice vectors are 90 ± 2°. Depending on composition and pore size, the structures contain between 192 units of SiO_2 and 320 units of dense $Si(CH_2)_2$. We use the theoretical model of $Si(CH_2)_2$ as a counterpart of the SiC:H sample used in the experimental study. The modeling procedure and resulting model properties are discussed in detail in [6].

For this study, we employ five different types of structural models, which correspond to the different experimentally examined materials. Dense, defect free SiO_2 corresponds to the amorphous SiO_2 sample; dense defect free SiCOH at 25 at.% C corresponds to sample DS; dense, defect free $Si(CH_2)_2$ corresponds to SiC:H sample; and model of SiCOH containing pores of ~1.0 nm diameter,

Table 1
The relative elemental concentration[a], porosity and static dielectric constant of the studied low-k dielectric samples.

Sample name	Sample type	Static dielectric constant	Porosity (%)	Relative content of Si, O and C (%)		
				Si	O	C
DS	Dense SiCOH	3.1	0	31	46	23
PS1	Porous SiCOH	2.2	11.8	26	38	36
PS2	Porous SiCOH	2.0	36.5	34	44	22

[a] Amount of hydrogen is not included.

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