

Research paper

Effect of deposition technique on chemical bonding and amount of porogen residues in organosilicate glass

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ABSTRACT

Impact of deposition technique on the chemical bonding in low- κ organosilicate glass (OSG) films and on porogen residues was studied using near edge X-ray absorption fine structure (NEXAFS) and internal photoemission (IPE) spectroscopy. The carried analysis reveals that self-assembly technology (SAT) allows one to obtain OSG-films without carbon residues, i.e. with “a clean bandgap”. Conventional PECVD film contains appreciable amount of carbon clusters, which account for gap states responsible for charge trapping and leakage current.

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1. Introduction

A key point in multi-level metallization design consists in integration of low- κ material as inter-level dielectric (ILD) in order to reduce capacitive delays and power consumption [1]. Organosilicate glass (OSG) is a main low- κ material, which has been successfully integrated in almost all the 90 nm products starting from 2004 on [1,2]. The OSG films remain main contenders for application in later chip generations due to possibility of flexible structure engineering. The main route towards further permittivity reduction is based on creating porosity in the OSG layers [1]. Traditionally porosity is attained through co-deposition of the matrix SiCOH material with organic labile C_xH_y porogen precursor. Then the SiCOH- C_xH_y films have to be cured in order to remove C_xH_y porogen and form a porous structure. In principle an extremely low value of permittivity ($\kappa < 2.5$) [3] can be achieved by this way but considerable amount of porogen residues in the form of carbon clusters may remain in the structure [3]. The carbon clusters may cause an enhanced leakage current and, therefore, one still exploring advanced methods of creating porosity of OSG.

In this work we carried out a comparative analysis of structural properties of OSG films prepared by conventional plasma enhanced chemical vapor deposition (PECVD) method using labile organic porogen and by advanced self-assembly technique (SAT) without porogen applying. In porogen based PECVD method the resulting porosity is significantly disordered due to lack of ability to control the

placement of the organics used to create porosity in the dielectric material during deposition. Instead of organic porogen the polymer templates are used in SAT method, which self assemble to form nanostructures with well-defined size and narrow size distribution leaving no porogen residues in the structure.

2. Materials and methods

We analyzed low- κ OSG layers (thickness 180 nm) on p-Si(100)/SiO₂(1 nm) substrates prepared by two methods: i) self-assembly technology (SAT) ($\kappa = 2,0$) (without porogen) using polymer templates; and ii) conventional plasma enhanced chemical vapor deposition (PECVD) ($\kappa = 2,3$) followed by removal of sacrificial C_xH_y porogen using thermal-UV curing at 430 °C. The SAT low-k film was formed by condensing a hydrolyzed alkylated silica sol in the presence of a polymeric surfactant. This surfactant acts as a template to produce a regular porous structure as the film dries. In this method, the surfactant acts as a porogen and evaporates during thermal curing (400 °C), leaving behind a porous silica network with alkyl groups passivating the internal and external surfaces of the film [4]. The PECVD films were deposited at 300 °C from organosilane matrix precursor and sacrificial organic porogen and subsequently cured as described in detail elsewhere [5]. Mechanical properties (Young modulus and mechanical hardness) of these insulators were compared to other types of low-k films in [6] (cf. Table 1 in [6]).

These insulators were studied using near edge X-ray absorption fine structure (NEXAFS) and internal photoemission (IPE). NEXAFS arises from core electron excitation into unoccupied molecular orbitals states

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as a result of photoabsorption. Due to multiple scattering of the excited photoelectron on the nearest surrounding of the absorbing atom NEXAFS is highly sensitive to the nature, chemical state and local coordination environment [7]. The presented absorption spectra were calculated from the measured reflection spectra using the Kramers–Kronig relations as described in detail in the previously published works [8,9]. Measurements of the reflection spectra were performed at the BESSY II synchrotron light source at the Helmholtz-Zentrum Berlin using the Reflectometer station at the Optics beamline [10].

Finally, internal photoemission (IPE) spectroscopy enables interface barrier determination by observing photoemission of electrons from Si substrate or semitransparent (15-nm thick) Al electrodes thermoresistively evaporated on top of low- k insulator [11]. Furthermore, the photocurrent measurements can also be used to determine energies of carbon-related gap states from the spectral plots of quantum yield (Y) defined as the photocurrent normalized to the incident photon flux. More details on these measurements can be found elsewhere [7].

3. Results and discussion

The photocurrent yield spectra are shown in Fig. 1 for Al/OSG/Si capacitors with SAT (a) and PECVD OSG (b) films. Different energies of the photocurrent spectral thresholds observed under positive and negative bias V_g applied to the top Al electrode in samples with SAT film (panel a) indicate observation of electron IPE from the Al electrode (negative bias) and Si substrate (positive bias) which reflect different energy distribution of the occupied electron states in these solids. The arrows $\Phi(\text{Al-SiO}_2)$ and $\Phi(\text{Si-SiO}_2)$ indicate the corresponding energy barriers between the upper edge of the occupied electron states in the corresponding electrode, i.e. the Fermi level in Al and the top of the valence band in Si, and the bottom of conduction band of SiO_2 [12]. By contrast, PECVD film (panel b) exhibits the same energy onset and spectral distribution of the photocurrent for both bias polarities suggesting optical excitation of electrons to occur inside the insulating film. The spectrum of the photocurrent yield suggests the contributions of electron excitations with energy thresholds close to the electron IPE thresholds from sp^2 -bonded carbon clusters in continuous a-C:H films deposited onto SiO_2 [13]. Arrows in Fig. 1b indicate the corresponding energy barriers between the top of occupied states of wide-gap a-C:H and graphite-like carbon layers and the conduction band bottom of SiO_2 . It is instructive to compare these barriers to the position of Fermi levels of frequently used metals (Al, TiN, TaN) referenced to the bottom of conduction band in SiO_2 or low- k oxide insulators which is typically in the range between 3.0 and 4.5 eV [11,14]. This energy range overlaps with the energy range of gap states observed in porogen-based PECVD OSG insulator. From this observation one may conclude that the gap states induced by

carbon residues cover the whole energy range corresponding to the Fermi level energies typical for contact materials. The presence of the gap states may be correlated with the observed increase of the leakage current across the insulating layer from 10^{-11} – 10^{-10} A/cm² in the SAT samples to 10^{-9} – 10^{-8} A/cm² in PECVD OSG samples at the same strength of electric field of 1 MV/cm. In order to shed light on the nature of the gap states the OSG films were studied by NEXAFS method, which is directly sensitive to chemical composition of a specimen.

The $\text{SiL}_{2,3}(2p)$ -absorption spectra of PECVD and SAT films are shown in Fig. 2 together with the reference spectra of α -quartz and amorphous SiO_2 . In general, the main structural unit of SiO_2 compounds and OSG is SiO_4 and $\text{SiO}_4 - n(\text{CH}_3)_n$ tetrahedron, respectively. Within the quasi-molecular approach, the main fine structure features **a-a'**, **b** and **c** in the shown $\text{SiL}_{2,3}(2p)$ -absorption spectra (Fig. 2) can be associated with the transitions from Si 2p-states to the $[\text{SiO}_4]^{-5}$ cluster excited states: a_1 (Si 3s-like), t_2 (Si 3p-like) and e (Si d-like) symmetry, respectively [15,16] (the double feature **a-a'** is due to 0.6 eV spin-orbit splitting of the initial Si 2p level). Note that feature **c** is associated with transitions to the e -continuum states and reflects the influence of the nearest surrounding (the molecular field of the oxygen atoms) on the silicon atom photoabsorption process. In turn, the **c'** and **c''** features in the $\text{SiL}_{2,3}(2p)$ -absorption spectrum of α -quartz reflect the presence of the long-range order in the α -quartz crystal [16]. Consistently with this interpretation, these features virtually disappear in the spectrum of the amorphous SiO_2 due to lack of the long-range order in its structure. Combined analysis of the $\text{SiL}_{2,3}(2p)$ spectra reveals significant broadening of the feature **b** when starting from α -quartz to am- SiO_2 , and further to OSG films. In the last case the additional broadening might arise due to porosity of the OSG structure which leads to further network distortion. Furthermore, in the spectra of OSG the shape of feature **b** is quite asymmetric while the main peak **b'** is seen to be shifted by 0.5 eV towards the lower energy relative to the peak **b** in the spectra of α -quartz and am- SiO_2 . This effect might be due to insertion of $-\text{CH}_3$ methyl groups in the some of the SiO_4 tetrahedra units. The incorporation of $-\text{CH}_3$ groups in the first coordination sphere of a Si-atom would lead to a decrease of positive effective charge on silicon due to smaller electronegativity of carbon atom as compared to oxygen resulting in the shift of the fine structure of $\text{SiL}_{2,3}(2p)$ -absorption spectrum towards a lower energy. Comparing the value of energy shift with the literature value [17] we can conclude that the main structural unit of both studied OSG films represents a $\text{SiO}_3(\text{CH}_3)$ tetrahedron with one methyl group inserted with no significant contribution of tetrahedra with multiple methyl unit insertion. The presence of considerable number of pristine SiO_4 tetrahedra in the structure of both OSG films can be traced from the observation of a shoulder **b** in the OSG $\text{SiL}_{2,3}(2p)$ -absorption spectra at 108.2 eV closely resembling the corresponding

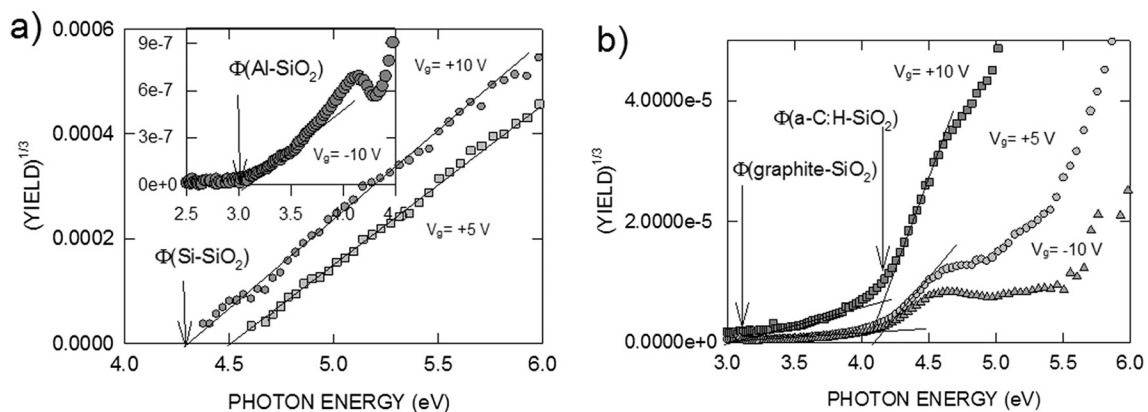


Fig. 1. Determination of spectral thresholds Φ using Powell ($Y^{1/3}-h\nu$) and Fowler ($Y^{1/2}-h\nu$) spectral plots of the electron photoemission quantum yield from Al (negative metal bias) and Si (positive metal bias) electrodes into OSG layers grown by self-assembly technique (SAT) $\kappa = 2.0$ (a) and PECVD method ($\kappa = 2.3$) (b). The spectra are measured when applying +5 V, +10 V and –10 V bias to the top Al electrodes.

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