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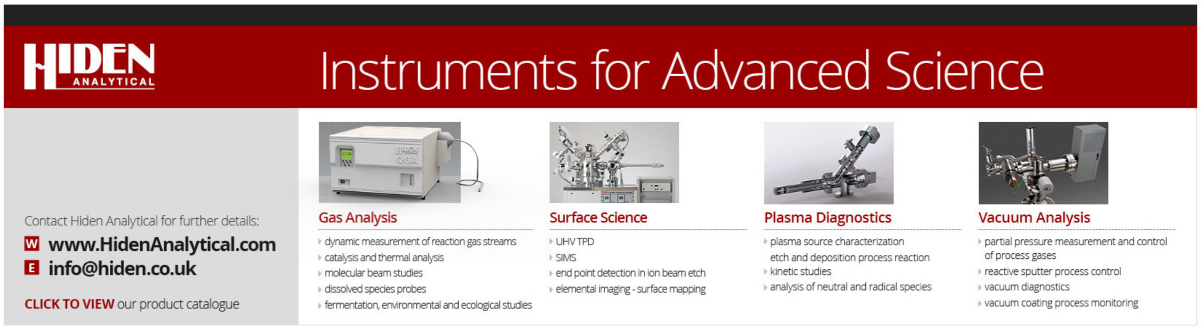

Extrinsic time-dependent dielectric breakdown of low-k organosilicate thin films from vacuum-ultraviolet irradiation

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In this work, the effect of vacuum ultraviolet (VUV) photon irradiation on the time-dependent dielectric breakdown (TDDB) of low-k organosilicate thin films was investigated, with particular emphasis on extrinsic TDDB (includes Cu migration effects). State-of-the-art low-k a-SiOC:H thin films were utilized because of their relevance as both an interlayer dielectric and as a candidate Cu capping-layer material. Synchrotron radiation was used to mimic VUV photon irradiation from processing plasmas without the presence of charged particles. TDDB characteristic lifetimes of the low-k a-SiOC:H dielectrics, before and after VUV photon exposure, were measured based on a Ti/a-SiOC:H/Cu metal-insulator-metal structure. The deterioration of extrinsic TDDB was observed in the film after exposure to VUV photons with 9 eV energy. The most notable degradation of the dielectric characteristic lifetime was found when the Cu electrode was used as an anode in the sample after 9.0 eV VUV photon exposure (photon fluence is 4.0×10^{15} photons/cm^2). This is believed to be related to the Cu^+ ions created by a VUV photon-assisted reaction. In the presence of an electric field, these Cu ions drift into the low-k dielectric and deteriorate TDDB performance.
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I. INTRODUCTION

To extend Moore's law as far as possible, back-end-of-the-line (BEOL) dielectrics, both intermetal and interlevel, with low dielectric constants (i.e., low-k) are needed to improve the performance of nanoelectronic Cu-interconnect structures in current and future ICs.[1] In the case of Cu-based metallization, metallic diffusion barriers (such as Ta and TaN) and dielectric capping layers (such as a-SiC$_x$N$_y$:H) are used to reduce Cu migration into the dielectrics[2,3] and to prevent electrical leakage between adjacent metal lines.[4] As aggressive shrinking of via and trench sizes continues, the reliability and yield issues associated with integration and implementation of such Cu/low-k dielectric interconnects are becoming more challenging than expected.[5,6] One critical challenge is the reliability of the interface between Cu and low-k dielectrics.[7,8] This is because (1) continuous technology scaling requires thinner and thinner capping layers, which have to be thinner than 1.0 nm or even 0.5 nm.[9] This may eventually make the barrier layers so thin that the Cu lines are effectively in direct contact with low-k interlayer dielectrics,[10] and (2) as technology continues to downscale, the relative contribution of the capping layer k-value to the interlayer capacitance is growing. Thus, there is a critical requirement for alternative materials with lower dielectric constants, since currently used capping layer materials (a-SiC$_x$N$_y$:H) have the highest k-values in conventional Cu interconnect structures.[11] For example, SiN has a k-value over 6.0,[12] and SiC and SiCN both have k-values between 4.0 and 5.0.[13,14]

Dense low-k a-SiOC:H (~2.0 g/cm^3) dielectric materials are being considered as alternative capping-layer dielectrics and have attracted much attention because of their significantly reduced k-values relative to conventional a-SiC$_x$N$_y$:H dielectric materials.[12] In either of the two scenarios described above, the low-k dielectric material will contact to the Cu wires directly.[11,12] One must therefore fully examine the electrical properties of the Cu/low-k interconnects even without the presence of a-SiC$_x$N$_y$:H capping layer.

In addition, the low-k dielectrics are exposed to multiple plasma-processing steps with the presence of photons [from deep vacuum ultraviolet (VUV) to infrared], energetic ions, electrons, and highly reactive radicals.[5,15] Plasma-induced damage degrades both the mechanical and electrical properties of low-k a-SiOC:H.[6] Due to the deep penetration depth and high fluence, VUV photons emitted from the plasma have been reported to cause failures of the Cu/low-k interconnects.[16,17] Very recent work shows that VUV photon irradiation deteriorates the *intrinsic* time-dependent dielectric breakdown (TDDB) (without including Cu-migration effects) of the a-SiOC:H thin films.[18] In this work, we will investigate the effects of VUV photon irradiation on the *extrinsic* TDDB (including Cu-migration effects) of low-k a-SiOC:H thin films.

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II. EXPERIMENT

To examine the extrinsic TDDB of the low-k materials, a-SiOC:H thin films with k-value of ~3.2 and density of ~1.5 g/cm^3, which have been used as interlayer dielectrics and are being considered as a candidate low-k capping layer dielectric, deposited on a Cu layer, are used in this work. The details of the deposition process and the a-SiOC:H film have been previously reported in detail.[7,8] In brief, the Cu thin films utilized for these experiments consist of electrochemically plated (ECP) Cu that is chemically mechanically polished (CMP) using a Cu ECP and a CMP process optimized for 32-nm interconnect technology. The ECP Cu was plated on a Cu seed and a TaN adhesion layer sputter deposited on 300-mm diameter Si (001) substrates on which 100 nm of thermal oxide had been previously grown. After Cu CMP, the final Cu thickness was 350 nm. The a-SiOC:H thin films were deposited with a thickness of 100 nm on the Cu by PECVD at temperatures on the order of 400 °C using a standard commercially available 300-mm PECVD tool. The precursor utilized is dimethoxydimethylsilane, $(CH_3)_2Si(OCH_3)_2$, diluted in He gas.[3] Prior to a-SiOC:H deposition, an H_2 plasma pretreatment was performed *in situ* to remove Cu corrosion inhibitors left behind by the Cu CMP process and to reduce Cu surface oxides formed by ambient exposure. Such plasma pretreatments are commonly performed prior to dielectric Cu capping-layer deposition on Cu interconnects in order to improve the electromigration performance of the dielectric/Cu interface.[19] No sacrificial porogen or post UV-curing were utilized. This inhibits moisture uptake of the samples by significantly reducing the concentration of the hydrophilic groups from porogen residuals in the dielectric. After deposition, the carbon concentration in the film bulk was approximately 14% (like a-$SiO_{1.2}C_{0.35}$:H).[7] These low-k/Cu stacks are well suited to study Cu migration into low-k a-SiOC:H from VUV irradiation.

Monochromatic VUV exposures were made using a synchrotron-radiation system described previously.[17] The incident VUV photon beam, with a cross-section of ~15 mm (horizontal) × 4 mm (vertical), was oriented normally to the surface of the sample at a pressure of 10^{-8} Torr. The beam was scanned vertically in eight steps with 1.5 mm step size over the surface of the film in order to achieve a nearly uniform exposed area of at least 10 × 10 mm. The VUV photon energy was set at 9.0 eV, because the reported penetration depth at these photon energies through amorphous silica-based dielectrics has been estimated to be ~200 nm.[20] Consequently, the entire bulk of the low-k dielectric can be modified with 9.0 eV VUV photon irradiation. The photon flux was monitored *in situ* using a photodiode (AXUV100) and the total photon fluence impinging on the sample was approximately 4.0×10^{15} photons/cm^2. This value is comparable to the total UV/VUV photon fluence of typical plasma exposure used in an actual plasma process.[17] During VUV irradiation, the substrate temperature of the film stack was monitored with a thermocouple connected to the back of the sample. The measurements show that the substrate temperature did not show significant changes during/after VUV irradiation.

After VUV exposure, the TDDB characteristics of the Cu/low-k interconnect were measured using a metal-insulator-metal (MIM) structure as illustrated in Fig. 1. A 100-nm thick titanium hexagonal pattern was deposited on the a-SiOC:H thin film using e-beam evaporation, followed by a layer of silver with a thickness of 200 nm. Since the diffusivity of Ti into a-SiOC:H is much smaller than that of Cu,[21] utilizing Ti electrodes can effectively avoid contamination of low-k dielectrics from metal diffusion. The purpose of the 200-nm Ag layer is to release the physical-stress pressure from the pin probe during electrical testing. The area of each hexagon is about 2.8×10^{-4} cm^2. The Cu layer underneath the a-SiOC:H was used as the other metal electrode, which is formed by sputtering off the low-k a-SiOC:H thin film using an Ar ion beam (3 keV). In such a Ti/a-SiOC:H/Cu MIM structure, if the Cu electrode is used as an anode, the electric field can drive Cu ions into the dielectric; when the Cu electrode is used as a cathode, drift of the Cu ions will not occur.[22]

Such a configuration, as shown in Fig. 1, enables one to examine the extrinsic TDDB of a-SiOC:H including the effect of Cu ion drifts. For each TDDB measurement, a constant voltage was applied across the sample between two pin probes connected to the electrodes, and the current was measured as a function of time until breakdown occurred. A temperature-controlled heater was used to heat the sample. The applied voltage was ramped at a rate of 1 V/s with a settling time of 250 ms until the desired voltage was reached. The voltage was then kept constant, and the leakage current was measured as a function of time. A failure criterion was set to be the point at which a sudden increase in leakage current of more than 3 orders of magnitude was observed, to be consistent with other TDDB measurements on low-k dielectrics.[18,23]

III. RESULTS AND DISCUSSION

Figure 2 shows Weibull plots of the extrinsic TDDB lifetimes for pristine and 9.0 eV VUV-exposed a-SiOC:H thin films. TDDB measurements were made under two sets of conditions: (1) using the Cu as an anode and (2) using the Cu as a cathode. Under both conditions, the electric field

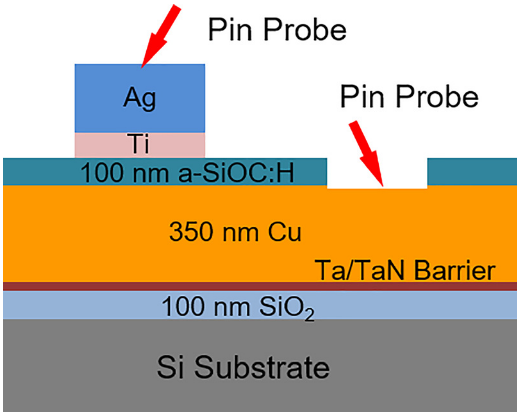

FIG. 1. (Color online) Schematic illustrating the Ti/a-SiOC:H/Cu MIM structure used for TDDB measurements.

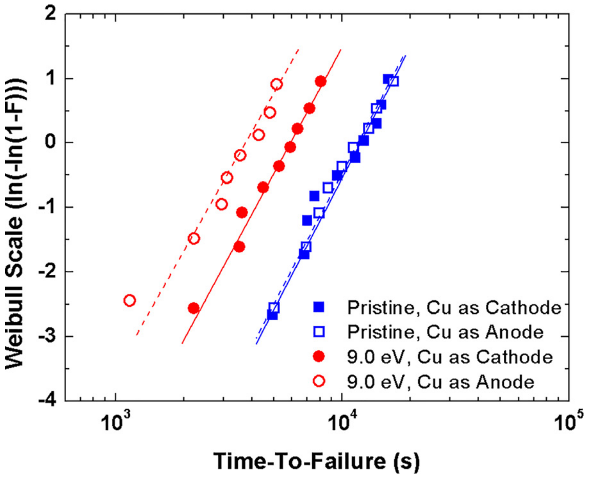

FIG. 2. (Color online) Weibull plots of the extrinsic TDDB lifetimes for pristine and 9.0 eV VUV-exposed a-SiOC:H thin films.

was 4.0 MV/cm and the temperature was 120 °C. Ten samples were measured for each case. As indicated in Fig. 2, for the pristine sample, no difference in the probability curve was observed whether the Cu was used as an anode or cathode. The calculated 63.2% time-to-failure of the a-SiOC:H film for the two cases (anode and cathode conditions on the Cu) do not display much difference. This result indicates that no Cu^+ ions exist in the pristine sample, which is reasonable because prior to SiCOH deposition, H_2 plasma pretreatment was performed *in situ* to remove any potential source of Cu^+ ions, such as Cu corrosion inhibitors.

However, TDDB degradation was observed for 9.0-eV VUV-exposed samples, as the probability curves are seen to move to the left. In addition, after 9.0 eV VUV irradiation, the TDDB curve measured using Cu as the anode deviates from that measured using Cu as the cathode, and the former shows a more severe degradation. This deviation indicates the generation of Cu^+ ions in the sample after 9.0 eV VUV photon exposure. To further verify this, and to examine the VUV-induced modification to the low-k a-SiOC:H dielectrics, XPS was performed on both the pristine and the VUV irradiated samples.

Figure 3 shows the core level XPS spectra of the Cu 2p, C 1s, Si 2p, and O 1s measured from the pristine and the VUV-exposed Cu/a-SiOC:H film stack. The Cu 2p core-level XPS data was obtained by sputtering (3.0 keV Ar ion) the top dielectric film away and by scanning over an area of about 1.5 × 1.5 mm to ensure a lateral homogeneous ion-current distribution. After each sputter step, core-level XPS spectra of the selected elements were recorded. The sample was rotated during sputtering to minimize sputter-induced roughening. All spectra were calibrated with reference to the C 1s peak at 284.8 eV.[24] The Cu 2p XPS spectrum from the pristine sample, as shown in Fig. 3(a), exhibits two major peaks at binding energies of 932.7 and 952.45 eV, which correspond to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ levels, respectively, revealing that the transported Cu in the a-SiOC:H exists primarily in the atomic state.[25] However, two satellite peaks were observed at 964.7 and 945.6 eV in the Cu 2p core-level spectra of the 9.0 eV exposed samples. These satellite peaks are from Cu oxides (CuO or Cu_2O),[26] indicating that part of the Cu transported into VUV-irradiated a-SiOC:H is in ionic form (Cu^+). Due to its electropositive characteristic, the migration of Cu^+ into a-SiOC:H will be accelerated

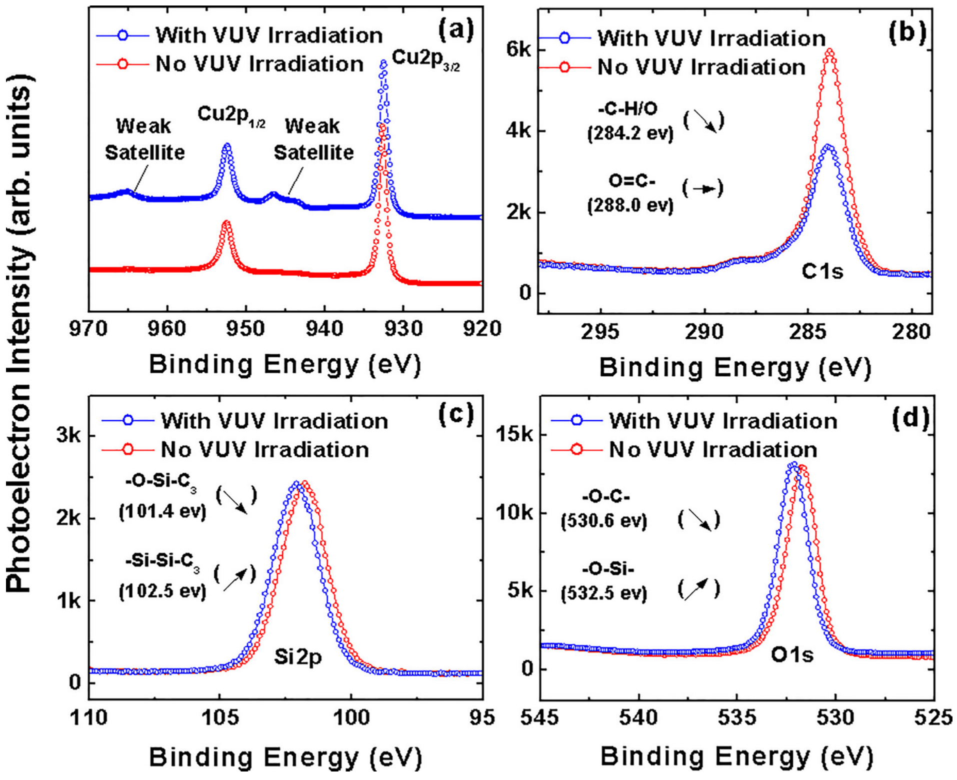

FIG. 3. (Color online) Core-level XPS of pristine and 9.0 eV VUV-exposed a-SiOC:H thin films.

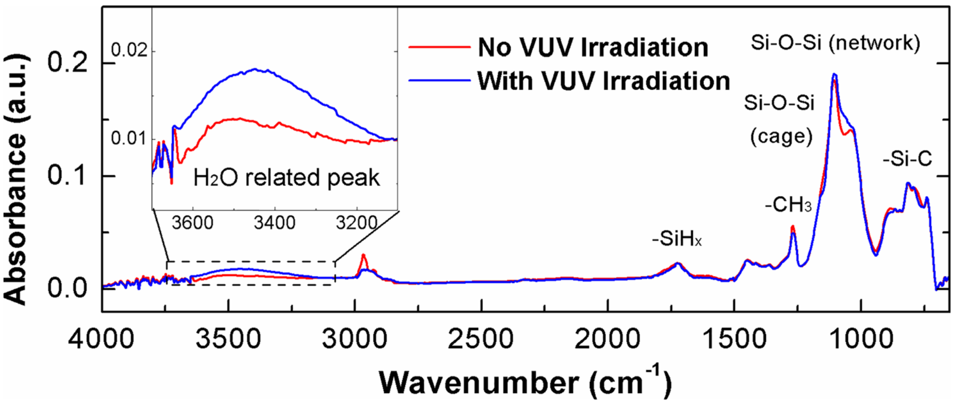

FIG. 4. (Color online) FTIR spectra of pristine and 9.0 eV VUV-exposed a-SiOC:H thin films.

by the electric field. Since there were no detectable Cu 2p satellite peaks for Cu inside pristine a-SiOC:H, the Cu^+ ions must be formed via a VUV photon-assisted reaction within the a-SiOC:H. The other significant impact of VUV exposure on the a-SiOC:H thin film is carbon depletion, as evidenced by the decreased intensity of C 1s XPS peak as shown in Fig. 3(b). The loss of carbon chemical groups, which are hydrophobic,[27] can cause the a-SiOC:H to be hydrophilic and absorb moisture from the ambient, once exposed to air.

Figure 4 shows the FTIR spectrum of pristine and 9.0 eV exposed a-SiOC:H (prior to deposition of the metal electrode), measured in an enclosure filled with dry N_2 gas. The results indicate a slight carbon loss and a structural rearrangement (i.e., conversion of the Si–O–Si bonds from cage to network) after VUV irradiation, which agrees well with the XPS measurement as described earlier. The broad band at higher wavenumbers of the FTIR spectrum is related to the formation of -OH groups and to the incorporation of water within the film, i.e., absorbed H_2O (3300–3600 cm^{-1}), stretching Si-OH (3200–3650 cm^{-1}), isolated and terminal -OH (3650–3800 cm^{-1}).[5] It was found that after 9.0 VUV irradiation, the peak intensity of the -OH related features increases moderately.

This agrees well with previous work,[8] in which we showed that after 9.0 eV VUV irradiation, hydroxyl ions (OH^-) will be generated in a-SiOC:H following a condensation reaction of two silanol groups (i.e., $\text{-Si-OH} + \text{-Si-OH} \rightarrow \text{-Si-O-Si-} + \text{-OH}^- + H^+$), and consequently form CuO/Cu_2O, acting as a Cu^+ ion source. Under the combined action of moderate temperature and an external electric field, the generated negatively charged hydroxyl ions (OH^-) and positively charged hydrogen ions (H^+) were able to diffuse within the dielectric film rapidly due to their higher mobility compared with that of sodium, copper, or other metals. Those hydroxyl ions (OH^-) that reach the Cu/dielectric surface may react with Cu to form $Cu(OH)_2$, which is not stable and can easily decompose to form CuO/Cu_2O. These formed metal oxides can become a source of Cu^+ ions that are available for migration in the presence of the electric field. For the 9.0 eV exposed samples, when the Cu was used as an anode, the Cu ions drift into the low-k dielectric in the presence of the electric field. According to the work of Suzumura *et al.*,[28] the drift of Cu^+ ions into a-SiOC:H forms a deep-level defect in the band gap of the material that acts as a generation-recombination center and is therefore detrimental to device lifetime. On the other hand, accumulation of the Cu^+ ions inside the dielectric may raise the local electric field to such an extent that the field exceeds the breakdown strength and thus promotes failure.[29]

IV. SUMMARY AND CONCLUSIONS

In summary, the effects of VUV photon irradiation on the extrinsic TDDB of a-SiOC:H, involving the effects of Cu migration, were examined. Results show extrinsic TDDB of a-SiOC:H deteriorates after 9.0 eV VUV irradiation and the most notable degradation of the characteristic lifetime was found when the Cu electrode was used as an anode in the VUV-exposed sample. It is believed to be related to the Cu^+ ions created by the 9.0-eV VUV irradiation. The results suggest that during the fabrication progress, the VUV photons from plasma processing can deteriorate the performance of BEOL Cu/low-k organosilicate interconnects. Thus, reducing exposure to high-energy VUV photons will be helpful in the processing of low-k materials.

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