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Citation: Applied Physics Letters **107**, 232905 (2015); doi: 10.1063/1.4937582
View online: http://dx.doi.org/10.1063/1.4937582
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APPLIED PHYSICS LETTERS **107**, 232905 (2015)

Measurements of Schottky barrier at the low-k SiOC:H/Cu interface using vacuum ultraviolet photoemission spectroscopy

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(Received 14 October 2015; accepted 29 November 2015; published online 10 December 2015)

The band alignment between copper interconnects and their low-k interlayer dielectrics is critical to understanding the fundamental mechanisms involved in electrical leakage in low-k/Cu interconnects. In this work, vacuum-ultraviolet (VUV) photoemission spectroscopy is utilized to determine the potential of the Schottky barrier present at low-k a-SiOC:H/Cu interfaces. By examining the photoemission spectra before and after VUV exposure of a low-k a-SiOC:H (k = 3.3) thin film fabricated by plasma-enhanced chemical-vapor deposition on a polished Cu substrate, it was found that photons with energies of 4.9 eV or greater can deplete accumulated charge in a-SiOC:H films, while VUV photons with energies of 4.7 eV or less, did not have this effect. These critical values were identified to relate the electric potential of the interface barrier between the a-SiOC:H and the Cu layers. Using this method, the Schottky barrier at the low-k a-SiOC:H (k = 3.3)/Cu interface was determined to be 4.8 ± 0.1 eV. © *2015 AIP Publishing LLC.*
[http://dx.doi.org/10.1063/1.4937582]

To prevent increased resistance-capacitance (RC) delays and capacitive power dissipation, back-end-of-the-line (BEOL) dielectrics with increasingly lower dielectric constants (i.e., low-k) are required in nanoelectronic Cu-interconnect structures.[1] In the case of Cu-based metallization, metallic diffusion barriers (such as Ta and TaN) and dielectric capping layers (such as a-SiC_xN_y:H) are used to reduce copper migration into the interlayer dielectrics and to prevent electrical leakage between adjacent metal lines.[2,3] The aggressive shrinking of via and trench sizes requires thinner and thinner barrier layers.[1] Continuous technology scaling may eventually make the barrier layers so thin that the Cu lines are in direct contact with the low-k dielectrics.[4] However, the reduced-k-value of interlayer dielectrics, typically produced with the introduction of nanoporosities, can seriously compromise the performance of an actual low-k/Cu interconnect.[5–7] One critical challenge is electrical leakage at the interface between Cu and low-k dielectrics, particularly as electric fields approach 1 MV/cm or greater for <10-nm technology nodes.[8,9] Since interfacial barriers can play an important role in determining the charge transport characteristics and the potential electrical leakage mechanisms between materials, there is a critical need to understand the fundamental electronic band alignment between low-k interlayer dielectrics and Cu lines.[10,11]

The other driving force that requires characterization of the band alignment between Cu/low-k dielectric interfaces is the need for reducing the k-value of the Cu capping/etch stop layer, since the capping layers (a-SiC_xN_y:H) typically have the highest k-values in conventional Cu interconnect structures.[2,3] For example, SiN has a k-value over 6.0,[2] and SiC and SiCN both have k-values between 4.0 and 5.0.[12–14] As technology continues to downscale, the relative contribution of the capping layer k-value to the interlayer capacitance is growing, and there is a critical requirement for alternative materials with lower dielectric constants. Recently, dense low-k a-SiOC:H ($\sim$2.0 g/cm^3) dielectric materials have attracted much attention because of their significantly reduced k-values relative to conventional a-SiC_xN_y:H dielectric materials.[11] Electron transport across the low-k capping-layer dielectric and the Cu-line interface, however, represents another possible leakage path for low-k/Cu interconnects, which brings a serious reliability challenge.[15] To fully explore the possibilities of line-line and/or layer-layer leakage, one must therefore also examine the band alignment between Cu and low-k a-SiOC:H dielectrics used both as interlayer and Cu capping-layer dielectrics. To address this issue, this work utilizes vacuum ultraviolet (VUV) photoemission spectroscopy to measure the Schottky-barrier potential at low-k a-SiOC:H/Cu interfaces.

In low-k a-SiOC:H dielectrics, VUV irradiation can cause photoinjection, photoconduction, and photoemission of electrons depending on the incident photon energy and the dielectric thickness.[16,17] Electrons can be excited into the conduction band from the valence band or from defect states in the bandgap of the dielectric and travel in the dielectric and/or the substrate depending on their energy.[18–20] When the irradiated photon energy is greater than the band-gap energy plus the electron affinity, electrons from the valence band and/or defect states in the bandgap of the dielectric can be photoemitted and escape from the film surface, leaving positive charges trapped within the dielectric.[16,19] When the photon energy is less than the bandgap (E_g) of the dielectric, some of the photons can penetrate into the substrate. Photogenerated electrons from the substrate that have energies higher than the substrate/dielectric barrier potential can be

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injected into the dielectric layer and deplete the dielectric's accumulated positive charge produced by photoemission.[17,20] The lowest photon energy having a charge-depleting effect should correspond to the potential barrier present at the substrate/dielectric interface.[16,21] The measured substrate/photoemission current usually changes with photon energy due to the excitation of electrons from specific electronic states to energies above the conduction band of the dielectric layer. By exposing the materials to monochromatic VUV radiation at low flux and changing the photon energy rapidly, VUV photoemission spectroscopy can made without significantly changing the charge in the materials. This allows a measurement of the photoemission current response as a function of energy for dielectric materials. Previous work has shown that VUV photoemission spectroscopy can be used to examine the charge repopulation and depopulation within the dielectric layer from VUV irradiation, with the advantage of *in-situ* measurement.[21] In this work, it will be shown that VUV photoemission spectroscopy is an effective way to measure the Schottky barrier of the a-SiOC:H/Cu interface. Specifically, the interfacial Schottky barrier can be obtained by recording the VUV photoemission spectra before and after VUV irradiation with specific photon energies.

To assess the value of the Schottky-barrier potential present at the interfaces between Cu and dense/non-porous a-SiOC:H-based interlayer and Cu barrier dielectric materials, plasma-enhanced chemical-vapor deposited (PECVD) low-k a-SiOC:H thin films (k = 3.3) on polished Cu thin film substrates were used here. The specific low-k a-SiOC:H was investigated in this study due to its relevance as both a interlayer dielectric and candidate Cu capping-layer material. The details of the deposition process and the a-SiOC:H film have been previously reported in detail.[4,11] 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 CMP process optimized for 32-nm interconnect technologies. 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 at 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. Prior to a-SiOC:H deposition, an H_2 plasma pre-treatment 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. The bandgap energy of the a-SiOC:H thin film was determined to be 8.1 ± 0.3 eV using X-ray photoemission spectroscopy (XPS).[9]

Monochromatic vacuum ultraviolet exposures were made using a synchrotron radiation apparatus described previously.[22] The incident VUV photon beam, with a cross-section of $3.0 \times 0.1\,cm^2$, was oriented normally to the surface of the sample at a pressure of 10^{-8} Torr. The photon flux was monitored *in-situ* using a photodiode (AXUV100) to ensure samples were irradiated with a specific dose. The photoemission current from the surface of the sample during VUV exposure was monitored with a Keithley 486 picoammeter. The VUV photoemission spectrum was measured before and after each VUV irradiation.

Figure 1 shows the 6.0 to 14.0 eV VUV photoemission spectrum obtained from the low-k a-SiOC:H dielectric previously exposed to 12 eV photons with several different doses. The energy of 12 eV was chosen because the investigated dielectric had a high photoemission efficiency at this energy.[21] During the photoemission spectroscopic measurements, the photon-beam exit slit from the monochromator was set to 30 μm so that the photon flux was approximately two orders of magnitude smaller than that for the 12 eV photon pre-exposures and did not significantly affect the measured characteristics of the dielectric layer. The photoemission current was normalized by dividing the measured photoemission current by the incident VUV photon flux measured with the calibrated photodiode.

As shown in Figure 1, when the photon irradiation dose increases, the magnitude of the VUV photoemission spectrum decreases and reaches a steady state when the irradiation photon dose is greater than 5.0×10^{15} photons/cm^2. This is because, with increasing VUV photon doses, most of the electrons have been photoemitted, and thus there are few electrons within the defect states available to be photoemitted when the VUV photoemission spectroscopy scan was made after VUV irradiation. On the other hand, a self-consistent electric field is induced by the trapped positive charges in the dielectric.[19,20] The self-consistent electric field increases with increasing VUV photon dose because the number of trapped charges increases. As the self-consistent electric field increases, photoemission is reduced.[19] However, the photoinjection of electrons from the substrate into the dielectric is assumed to be a constant during VUV irradiation, since it depends primarily on the dielectric-substrate interface-barrier energy and the photon flux reaching the substrate.[19,20] When the photoemission current was approximately equal to the photoinjection current, a steady state was reached. This indicates that no

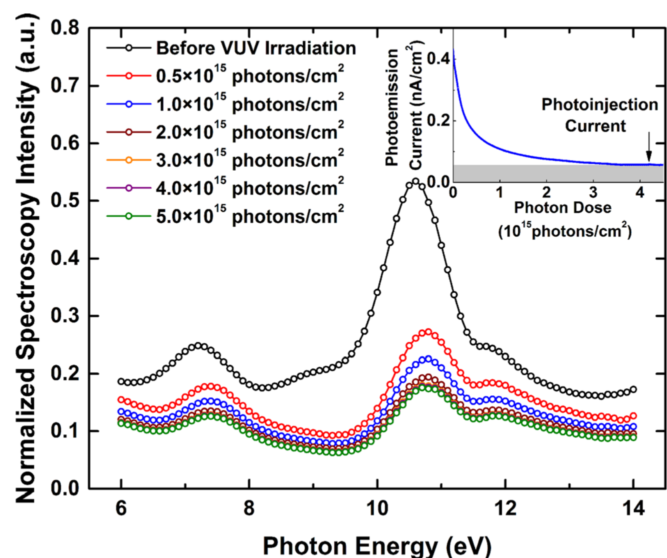

FIG. 1. VUV photoemission spectroscopy measured from a 100 nm low-k a-SiOC:H (k = 3.3) dielectric PECVD deposited on a H_2 plasma pre-cleaned Cu layer exposed to 12 eV photons with various doses; the inset is the photoemission current measured during 12 eV irradiation as a function of photon dose.

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more trapped charges will be generated in the dielectric, and the photoemitted electron flux will equal the flux of photoinjected electrons.[17,20]

The inset in Figure 1 shows the photoemission current measured during 12-eV irradiation. As expected, the photoemission current decreased with increasing photon dose and reached a steady level when the photon dose was 5.0×10^{15} photons/cm^2. It should be noted, however, that in addition to photoinjection, electrons can also move into the dielectric and/or undergo conduction through the dielectric by Fowler-Nordheim tunneling, where the tunneling current from the substrate is proportional to the number of interfacial defect states.[23] The injection current during VUV irradiation is therefore the sum of the photoinjection and tunneling currents. However, measurements of surface potential decay after irradiation prove that the leakage current is much smaller than the photoinjection current and therefore can be neglected.[19,20]

To investigate the photon-energy range that can repopulate the accumulated charge after 12 eV irradiation, each sample was re-exposed to VUV photons with specific energies from 4.5 to 8.1 eV in steps of 0.2 eV. A photon energy of 8.1 eV is approximately the bandgap energy of the low-k dielectric.[9] The VUV re-exposure was performed at the same location on the sample with the same photon dose of 5.0×10^{15} photons/cm^2, as was the case for the 12 eV exposure. VUV photoemission spectroscopy was re-measured after the second exposure. Figure 2 shows the photoemission spectroscopy after the second exposure of VUV photons over the range between 4.5 and 8.1 eV. Figures 2(a)–2(d) show the measured VUV photoemission spectroscopy of 12 eV irradiated samples with steady-state photoinjection followed with 4.5 eV, 4.7 eV, 4.9 eV, and 8.1 eV re-exposure with same photon dose.

As illustrated by these results, for sufficient 12-eV irradiation to reach steady-state photoinjection current samples, the experimentally measured VUV photoemission spectrum of the re-exposed samples with energies of 4.7 eV, or lower than that, overlaps and is nearly identical to that of the 12 eV irradiation to steady-state photoinjection current samples which was shown in Figure 1. However, for 4.9 eV and higher energy re-irradiated samples, there is an abrupt increase, at the scanning range (from 6.0 eV to 14.0 eV), in the photoemission spectrum. And when 8.1 eV photons were used for re-exposure, the largest increase in the spectrum was observed. In fact, the spectrum of 8.1 eV re-exposed samples is nearly identical to the VUV photoemission spectroscopy of an unexposed sample.

These effects can be explained by noting that electrons photoemitted from the Cu substrate produced by photons with energies less than 4.7 eV do not have sufficient energy to overcome the a-SiOC:H/Cu interface barrier to be injected into a-SiOC:H dielectric. Thus, they are not able to repopulate the traps in the dielectric that were depopulated during the 12 eV exposure. Therefore, the VUV photoemission spectrum is identical to that for the 12-eV irradiated samples, which had reached steady state of photoinjection. However, if the photoemitted electrons from the Cu substrate have energies larger than the potential barrier present at the a-SiOC:H/Cu interface, they can be injected into the dielectric and then refill defect states within the dielectric. This provides electron sources that can be photoemitted during the VUV spectroscopic scan, making the intensity of the VUV photoemission spectrum increases, like that shown in Figures 2(c) and 2(d). On the other hand, the electrons injected from the substrate will deplete the accumulated positive charge in the dielectric layer, and thus the self-consistent electric field will be reduced. The lower self-consistent electric field increases the photoemission, as discussed previously. This is what makes the intensity of the VUV photoemission spectrum increases. Therefore, the

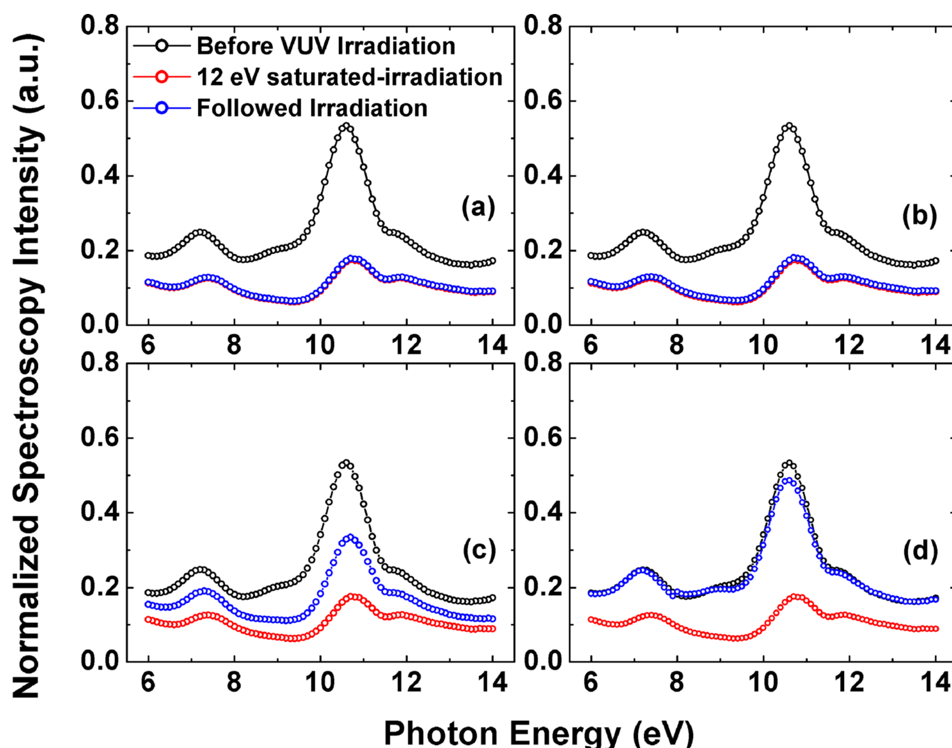

FIG. 2. VUV photoemission spectroscopy measured on a 100 nm low-k a-SiOC:H (k = 3.3) dielectric PECVD deposited on H_2 plasma-precleaned Cu layer before and after 12 eV exposure followed by re-irradiation under varied energies with a photon dose of 5×10^{15} photons/cm^2. The re-irradiation photon energies are (a) 4.5 eV, (b) 4.7 eV, (c) 4.9 eV, and (d) 8.1 eV, respectively.

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potential of the Schottky barrier at a-SiOC:H (k = 3.3)/Cu interfaces should be between 4.7 eV and 4.9 eV, that is 4.8 ± 0.1 eV.

To examine the validity and accuracy of the above values, the method of Grant and Waldrop,[24] which relies on core-level and valence-band XPS measurements, was also utilized to measure the Schottky barrier present at the same a-SiOC:H (k = 3.3)/Cu interface.[11] By referencing the XPS Si 2p core level of the low-k a-SiOC:H to its valence band maximum and then measuring how the position of the core levels changes with the addition of Cu, the Schottky barrier present at the a-SiOC:H (k = 3.3)/Cu interface was determined to be within a range of 4.7 eV to 5.2 eV. This value is consistent with the result obtained using VUV photoemission spectroscopy in this work.

In summary, VUV photoemission spectroscopy has been used to investigate the existence and magnitude of the Schottky barrier present at the interface of low-k a-SiOC:H/Cu interfaces. The Schottky-barrier potential at the a-SiOC:H (k = 3.3)/Cu interface was found to be 4.8 ± 0.1 eV. This proposed method of VUV exposure/re-exposure followed by VUV photoemission spectroscopy has been proved valid and efficient by showing consistency between the measured results and with previously reported values.

This work was supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and by the National Science Foundation under Grant No. CBET-1066231.

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