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Nonthermal combined ultraviolet and vacuum-ultraviolet curing process for organosilicate dielectrics

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Porous SiCOH films are of great interest in semiconductor fabrication due to their low-dielectric constant properties. Post-deposition treatments using ultraviolet (UV) light on organosilicate thin films are required to decompose labile pore generators (porogens) and to ensure optimum network formation to improve the electrical and mechanical properties of low-k dielectrics. The goal of this work is to choose the best vacuum-ultraviolet photon energy in conjunction with vacuum ultraviolet (VUV) photons without the need for heating the dielectric to identify those wavelengths that will have the most beneficial effect on improving the dielectric properties and minimizing damage. VUV irradiation between 8.3 and 8.9 eV was found to increase the hardness and elastic modulus of low-k dielectrics at room temperature. Combined with UV exposures of 6.2 eV, it was found that this "UV/VUV curing" process is improved compared with current UV curing. We show that UV/VUV curing can overcome drawbacks of UV curing and improve the properties of dielectrics more efficiently without the need for high-temperature heating of the dielectric. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4954176]

To fabricate high-speed ULSI devices, low dielectric constant (low-k) dielectrics are utilized in the back-end-of-the-line (where the transistor is connected to the rest of the integrated circuit) to reduce signal-propagation delay.[1] To reduce the dielectric constant of insulators to an even lower value, porous organosilicate low-k dielectrics (SiCOH) are used in fabricating the Cu/low-k structure to substitute for traditional Al/SiO_2 technology.[2] The techniques used are plasma-enhanced chemical-vapor deposition (PECVD) using porogen incorporation.[3,4] The porogens are removed with a post-deposition treatment, such as thermal annealing and ultraviolet (UV) curing, resulting in a porous SiCOH film with low-k properties.[5] The mechanisms of UV curing have been widely investigated.[6] Specifically, CH_x dissociation and Si-O-Si cross-linking enhancement contributes to the phenomena of porogen removal and improvement of mechanical properties in low-k thin films.[7] However, due to Si-CH_3 scission during UV curing, a tradeoff between strengthening mechanical properties and reducing the dielectric constant exists: a longer UV-curing time achieves better mechanical strength but increases the dielectric constant. Furthermore, UV curing requires concomitant thermal heating, which can result in deterioration of the films.

In this work, it will be shown that multi-energy photon irradiation in both the UV and Vacuum ultraviolet (VUV) regions (6.2 eV and 8.8 eV, respectively) can improve the electrical and mechanical properties of low-k dielectrics simultaneously and overcome the drawback of UV curing without the need for thermal processing. By comparing the performance of industrial UV curing and UV/VUV curing, it was found that the optimized UV/VUV-cured samples could achieve a lower dielectric constant compared with UV-cured samples. In the meanwhile, the mechanical properties after this processing are also improved. These investigations show that the optimum photon energies for post-deposition treatment of SiCOH exist as a combined UV/VUV process that can be utilized as a next-generation curing method for low-k material deposition technologies.

The selection of the particular wavelengths of the photons is the most important parameter for low-k dielectric curing.[8] It is determined by comparison with the dissociation energy of chemical bonds in the SiCOH matrix structures. In previous work, it has been shown that C-Hx dissociation energy was around 5.9–6.0 eV (Ref. 9) and Si-O conversion energy was approximately 8.3 eV.[10] In this work, samples were irradiated with monochromatic VUV synchrotron radiation. The advantage of a synchrotron is that it generates radiation with no charged particles and can be varied over a continuum of photon energies. This provides direct information on how photon irradiation affects the properties of porous low-k thin films. Here, SiCOH samples were exposed to various photon energies from 6.0 to 8.9 eV in steps of 0.1 eV. Energies higher than 8.9 eV will cause significant charge accumulation[11] and damage the dielectrics so were eliminated.[11] Then, the optimum photon energy ranges that can simultaneously improve electrical and mechanical properties of low-k thin films could be found.

The VUV photon beam was oriented to be normally incident on the surface of 640-nm low-k porous SiCOH samples ($k = 2.65$) at a pressure of 10^{-8} Torr. The samples used in this work were plasma-enhanced chemical-vapor-deposited

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(PECVD) on ⟨100⟩ *p*-type silicon wafers and deposition took place in a capacitively coupled PECVD reactor utilizing a 13.56 MHz RF source in the presence of several inert and reactive gases with an organosilane precursor. The VUV beam on the surface of the wafer had a cross-sectional area of $2.5 \times 0.1\,\text{cm}^2$ and the exit slit width of the synchrotron beam monochromator was set to $500\,\mu$m to maximize the photon flux. The accumulated photon fluence for each exposure was chosen to be 1×10^{15} photons/cm^2, which is comparable to the VUV photon fluence emitted during a typical plasma process.[12–14] The dielectric constant was obtained from capacitance-voltage (C-V) characteristics of the SiCOH samples measured with a Signatone H-150 W probe station. Mechanical properties such as elastic modulus and hardness of the tested samples are obtained from nanoindentation measurements. It must be mentioned that the hardness measurements for UV-cured SiCOH are complicated. The hardness of UV-cured SiCOH increases and then decreases with the increased indentation depth thus forming a peak. It is not clear at present about the mechanism that causes the hardness parameter to first increase and then decrease at small indentation depths. Wang and Grill[15] hypothesized that this phenomenon is caused by the non-uniform distribution of pores within SiCOH after curing. That is, if there are more pores at a layer near the surface of SiCOH, the measured hardness will be small. Then, if the indentation depth increases, and there are fewer pores in the deeper layers of SiCOH, the measured hardness will be higher. If the indenter moves further within the thin low-k films, and if there are more pores in the even deeper layers of SiCOH, the hardness will decrease again.[15] Another possibility is that the phenomenon might due to the nanoindenter crushing the pores and increasing the density as it moves deeper into the sample.[10] It is much like an airplane wing moves through the air or a boat going through the water: for airplane wing, the air compression changes with distance in front of the wing, and for the boat, water could occupy a larger volume in front of the boat but then it swells up.[10] Therefore, the hardness of UV-cured SiCOH increases and then decreases with the increased indentation depth.[10] Since there is no porosity (pores) present in uncured samples, as-deposited SiCOH does not exhibit this phenomenon.

A probe station (Signatone H-150 W) with a low-power optical microscope was used to make contact with a fabricated Metal-Insulator-Silicon (MIS) structures for all of the electrical measurements in this project. This probe station consists of three movable micropositioners with 5-μm diameter tungsten probe tips (Signatone SE-T).[16] Multiple titanium hexagonal metal dots, with an average area of $4.7 \times 10^{-4}\,\text{cm}^2$, were deposited on the surface of the dielectric to form a Metal-Insulator-Silicon (MIS) structure. Electrical contact is made to the semiconducting substrate by connecting one of the tungsten probes to the wafer platen. Electrical contact to the metal pads is made by carefully lowering the tungsten probe tip to the metal surface. The probe tip was held at an oblique angle relative to the sample surface to minimize damaging the electrode by the sharp point of the tip.[17] Specific care was taken to ensure that stray light and electrical noise did not influence any of the measurements. This was accomplished by placing an electrically shielded dark box over the entire probe station for each measurement.

For current-voltage measurements, a computer-controlled combination high-voltage supply and picoammeter was used (Keithley 6487) while for capacitance-voltage measurements an HP 4285A precision inductance-capacitance-resistance (LCR) meter is utilized instead. The measurements of the MIS C-V characteristics were made in the high-frequency regime (~1 MHz).

The elastic modulus (E_s) and Meyer hardness (H) of SiCOH films were investigated with a Hysitron (Minneapolis, MN, USA) TriboIndenter equipped with a Berkovich probe and operated in an open-loop mode. The machine compliance was evaluated using data from a series of indents with different loads placed in the center of a fused-silica standard and the SYS correlation.[18] Both calibration and SiCOH experiments utilized a load-control indent consisting of an initial 20-nm lift-off and re-approach in order to define the initial contact point accurately. This was followed by a 5s loading, a 5s hold at maximum load (P_{max}), a 2s unloading to 40% of the P_{max}, a 60s hold at 40% P_{max} to remove thermal-drift effects, and a 1s final unload. After correcting the fused silica load-depth traces for machine compliance, a series of indents were used to calculate the area function[19] following the standard Oliver-Pharr method.[20] All nanoindentation experiments were carried out at room temperature in air ambient.

It should be noted that since the usual nanoindentation procedures rely on hardness (H) and elastic modulus (E_{eff}) readings generated by the nanoindentation instrument based on the penetration depth and indenter shape, the substrate of a thin film will have an increased effect on H and E_{eff} as the penetration depth increases. For thin films deposited on a hard substrate, as is the case of porous low-k films on a Si substrate, the results are usually overestimated and unconvincing if the effects of the hard substrate are not considered. Also, for the porous structure of SiCOH, film densification underneath the probe could be significant during the indentation process, which brings additional challenges to nanoindentation analysis. To solve these problems, Stone's algorithms[19] were utilized to compare the experimental nanoindentation measurements as a function of indent size with Stone's theoretical simulations.[21]

The thickness of the dielectric layer was measured with a Filmetrics F-20 Optical reflectometer in the clean room at the Wisconsin Center for Microelectronics (WCAM) and confirmed with a Rudolph AutoELII-Vis-3 ellipsometer in the Soft Material Lab (SML) at the University of Wisconsin-Madison College of Engineering.

Figure 1 shows the dielectric constants of the test samples after VUV exposure compared with pristine and UV-cured samples. Figure 2 shows the changes to the elastic modulus (E_s) of the samples after VUV exposure, again compared with pristine and UV-cured samples.

Since 6.2 eV-exposure achieved the best performance to lower the k value of SiCOH[10] while 8.8 eV VUV exposure exhibited the best improvement in the elastic modulus, the performance of these monochromatic-irradiation-cured tested samples were compared with conventional UV-cured samples and are shown in Table I.

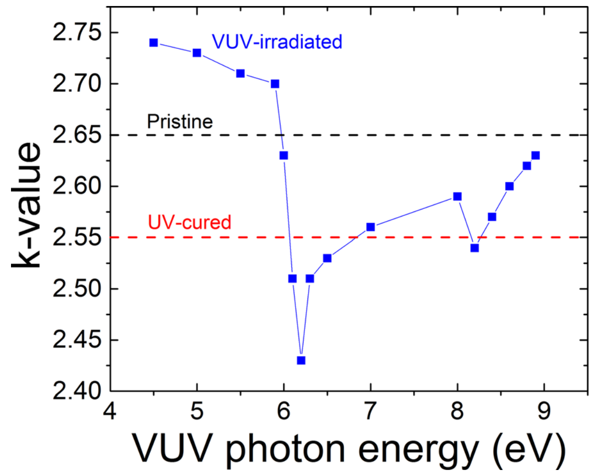

FIG. 1. Dielectric constant of VUV-irradiated samples. Pristine and UV-cured samples are shown with dashed lines.

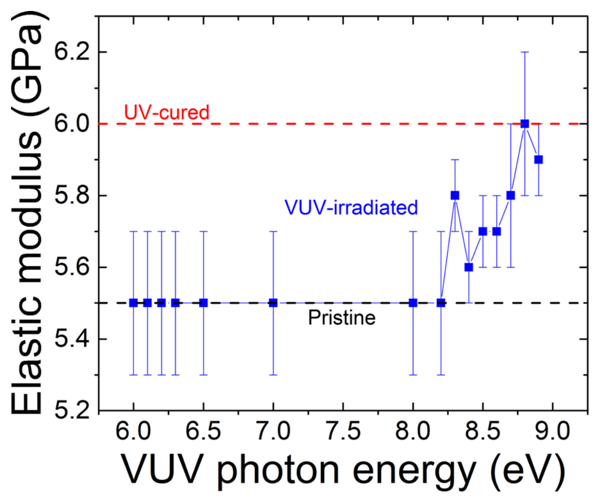

FIG. 2. Elastic moduli of VUV-irradiated samples. Pristine and UV-cured samples are shown with dashed lines.

The improvement of the electrical and mechanical properties is due to porogen removal and strength enhancement of the backbone structures of the low-k tested samples.[8,10]

It was found that none of the monochromatic VUV exposures were able to improve the electrical and mechanical properties of tested low-k dielectrics simultaneously. That is, the lower energy curing (6.2 eV) could achieve a much lower k value compared with UV-cured samples. However, this energy is not sufficient to improve the mechanical properties of the sample. Instead, 8.8 eV photons could improve the mechanical properties of the low-k thin films at a level comparable to UV-cured samples, but here the k value is much higher due to carbon loss (methyl dissociation) and incomplete porogen removal.[10] Therefore, a multi-step VUV curing was determined to achieve the goal of improving both electrical and mechanical properties simultaneously without the need for thermal heating.

TABLE I. Comparison of monochromatic VUV curing and UV curing (photon fluence 10^{15} photons/cm^2).

	K value	Elastic modulus (GPa)
6.2 eV exposed	2.43	5.5
8.8 eV exposed	2.62	6.0
UV cured	2.55	6.0

TABLE II. Comparison of optimized multi-step UV/VUV curing and UV curing (photon fluence 10^{15} photons/cm^2).

	K value	Elastic modulus (GPa)
8.8 eV + 6.2 eV exposed	2.51	6.0
Industrially UV cured	2.55	6.0

The multienergy method is described as follows. First, the samples were exposed to 6.2 eV photons to remove the porogen residues. Then, the samples were re-exposed to 8.8 eV VUV photons to enhance the mechanical properties of low-k dielectrics. Again, it must be mentioned that no thermal heating was used.

The results are shown in Table II.

Using this method, it was found that multi-step UV/VUV curing can achieve the mechanical property improvement of low-k dielectrics that is comparable to UV-curing while the k value is much lower. It must be mentioned that the curing performance of inverting the order of exposure, i.e., 6.2 eV + 8.8 eV and 8.8 eV + 6.2 eV irradiation was tested and the order of irradiation did not affect the experimental results. However, it is still recommended to first irradiate with UV (6.2 eV) followed by VUV (8.8 eV) irradiation since lower k is always the most important issue for SiCOH and the UV wavelength might lower k without inducing bad effects such as methyl group dissociation. If this methodology is practical in industrial applications in the near future, the "first UV then VUV" curing is still recommended. As a result, porogen removal could be tracked during the UV irradiation in the first step without changing any methyl, Si-O, and other related chemical bonds. Once the porogens are removed, then the photon irradiation should be switched to the VUV range to improve the mechanical properties. If VUV irradiation is undertaken at first, the relatively high-energy VUV photons could start to break chemical bonds and *in-situ* measurements or testing will not be helpful. Therefore, UV/VUV curing is recommended.

Moreover, the IV characteristics show that the multi-step cured SiOCH achieved a lower leakage current and higher breakdown voltage compared with the UV-cured samples. The result is shown in Figure 3.

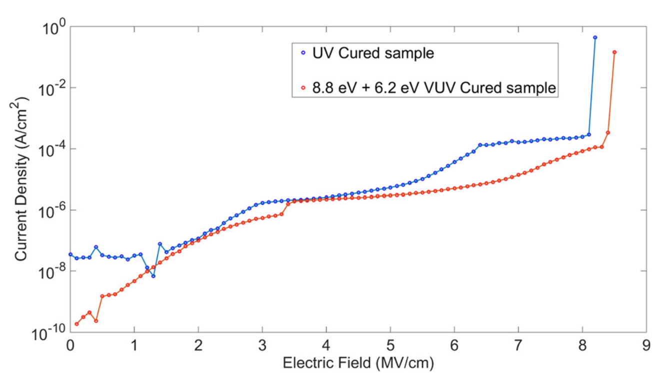

FIG. 3. Comparison of leakage currents and breakdown voltages for UV cured and UV/VUV cured SiCOH.

For each IV curve, seven test structures were measured and averaged to minimize experimental error. UV/VUV cured SiOCH shows an increase in the breakdown voltage (V_{bd}) of the SiCOH sample compared with the industrial UV-cured low-k SiCOH samples (427.5 ± 2.5 V versus 395 ± 5 V). This is believed due to the sufficient removal of porogens in low-k thin films since the conductivity of porogen residues is much higher than the backbone of low-k dielectrics.[21–27]

In summary, the optimized UV/VUV condition to cure as-deposited samples shows that after 6.2 + 8.8 UV/VUV irradiation with no thermal heating, UV/VUV curing has a better curing performance compared with industrial UV curing and could be a candidate for a potential future generation in semiconductor processing.

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