Radiation Effects in Low-Dielectric-Constant Methyl-Silsesquioxane Films

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Abstract — The use of state-of-the-art microelectronic devices in space radiation environments faces new challenges with the adoption of low-k materials as interlevel dielectrics. This is demonstrated in a preliminary study of methyl-silsesquioxane (MSSQ) films. We report radiation damage induced by a 2 keV low-current-density (-2×10^4 x^-1 cm^-2) positron beam and observed by positron annihilation spectroscopy.

Keywords — radiation damage; low-k dielectrics; polymer; low-energy; positron beam.

I. INTRODUCTION

The performance in state-of-the-art microelectronic devices can no longer be improved predominantly through miniaturization of the device components as in the past. To realize future progress, the semiconductor industry has been forced to undergo an historic evolution, adopting the use of new materials such as Cu interconnects, low-dielectric-constant (low-k; k < 3.0) interlayer dielectrics (ILD), metal diffusion barriers, high-k materials for capacitors and gate dielectrics, etc. [1]. Following the Cu technology, the implementation of the low-k dielectrics holds the key for future advances. The quest for the successful low-k ILD candidate is focused mainly on silicates and polymers (organic, inorganic, and their hybrids) with no prior use in the semiconductor industry. Spin-on and sol-gel fabrication methods are replacing the currently used chemical vapor deposition techniques. This enables the development of methods for incorporating porosity (k = 1) in the dielectric matrix, which is the only alternative to lowering further the dielectric constant (to k ~ 2.1 and below). Low-k dielectrics are entering production at the present (at the 130 nm technology node), whereas the implemented of their porous variants is expected at the 90 nm generation.

The ever-increasing trend of using commercial off-the-shelf (COTS) microcircuits in satellite and spacecraft systems, and the inevitability of low-k dielectrics replacing the SiO2 in COTS parts, necessitate an evaluation of the performance of such materials in space environments. Their properties can be critical for the device performance in a high radiation environment regardless of the circuit architecture.

Materials behavior under irradiation can be assessed using test structures and blanket low-k films. This can provide valuable information, which does not depend on the maturity of the low-k technology, or the device design, as would be testing of actual microcircuits. For this end, we studied porous methyl-silsesquioxane (MSSQ) films. MSSQ is one of the most studied ILD candidate with a high commercialization potential.

We used positron annihilation spectroscopy (PAS) to detect the radiation damage. This technique is extremely sensitive to open-volume defects (from vacancies to large pores) due to the propensity of a positron to "seek" defects, in contrast to common (electron, x-ray, neutron, etc.) scattering techniques. PAS is an established tool for characterization of free-volume in bulk polymers [4,5]. Recently, PAS gained industrial recognition [6-11] and is utilized by SEMATECH as a porosity characterization tool for low-k dielectrics. The effects reported in this work were first noted in such porosity characterization studies. Despite the widely accepted non-destructive nature of PAS [2,3], radiation effects were noted in studies of polymers [12,13].

II. EXPERIMENTAL

A. Positronium as a Probe for Porous Dielectrics

Positron beams with tunable energy (0–70 keV) [2] have a depth-profiling capability and are used to study thin (μm) films. In analogy with electrons, positrons injected in a solid loose their initial energy predominantly through ionization. For incident energies in excess of 1 keV, the positron and electron implantation profiles are virtually identical [14,15]. Therefore, a material, exposed to a positron and an electron beam with a given energy, receives equal radiation doses.

A positron reaches thermal equilibrium with the material within 1-2% of its lifetime, the remainder of which is spent in a state of thermal diffusion. During this time a positron probes the surrounding electronic environment until it eventually annihilates with an electron, giving off radiation (typically two 511 keV photons), which leaves the material without further interaction. These photons carry information about the electron momentum (measured through the Doppler shift or deviation from the 180° angle) and electron density (measured through the positron lifetime).

In dielectric materials, thermalized and low-energy (~1 eV) positrons can form a hydrogen-like bound state with an electron – positronium (Ps). Like hydrogen, Ps forms in two states: para-Ps (p-Ps; ↑↓ electron-positron spin configuration) and ortho-Ps (o-Ps; ↑↑). Their annihilation characteristics are
drastically different. The annihilation in the $\uparrow\downarrow$ state is fast ($\sim 8 \times 10^9 \text{ s}^{-1}$) and occurs predominantly via 2 photons ($2\gamma$). The $2\gamma$-channel is forbidden for parallel spins ($\uparrow\uparrow$) because angular momentum cannot be conserved — leading to a dominant higher-order $3\gamma$-annihilation process, with a significantly smaller rate ($\sim 7 \times 10^6 \text{ s}^{-1}$). The resulting $p$-Ps and $o$-Ps lifetimes in vacuum are 0.125 ns and 142 ns, respectively [16]. The $p$-Ps lifetime changes little in solids, whereas the $o$-Ps lifetime is shortened by the so-called "pick-off" ($2\gamma$) annihilation with molecular electrons of opposite spin to that of the positron. This pick-off lifetime, which spans two orders of magnitude (1-142 ns), and the $o$-Ps decay mechanism ($2\gamma$ or $3\gamma$) make the Ps a unique probe for porous materials [4-11]. However, the presence of unpaired electrons at the walls of a pore (e.g., from free radicals, broken or dangling bonds) can alter dramatically the annihilation signatures of $o$-Ps trapped in that pore [17-19]. Such scenario enhances strongly the pick-off annihilation rate.

B. Samples and Experimental Details

Thin (~0.7 µm) mesoporous MSSQ films were fabricated by the sacrificial porogen technique [20]. Si wafers were spin-coated with a solution containing low molecular weight MSSQ resin and volatile polymer additive (porogen, or porogen). The samples were treated thermally in steps first (at 200 °C) to vitrify the MSSQ without affecting the porogen, and then (at 450 °C) to decompose the porogen, which leaves voids embedded in the MSSQ network. The studied films, designated as A and B, contained approximately equal porosity fraction (~20%), but were produced using different resins and porogens. Both films had a density of ~1.05 g/cm$^3$.

The MSSQ monomer is generalized as $T = CH_3SiO_3/2$. Characteristic for the MSSQ polymerization are cage-like structures (T6, T8, etc.) or ladder-like chains. In reality, however, the MSSQ network is not as well defined, and both of these structures coexist.

A monoenergetic low-current (~30 fA; ~2×10$^5$ e'/s) positron beam, with a diameter of approximately 3.5 mm (a flux of ~2×10$^5$ s$^{-1}$cm$^{-2}$), was used to simultaneously irradiate the samples and to probe the porosity for up to 50 hours. Depth-profiles of the $o$-Ps annihilation signatures were taken by means of varying the beam energy; however, no depth-dependent effects were noticed. For the reported here measurements, the beam energy was set to 2 keV in order to maximize the $o$-Ps signal from the MSSQ films. The $o$-Ps lifetime and intensity, and its $3\gamma$-annihilation signal were monitored as a function of the exposure time.

III. RESULTS

Fig. 1 shows the $3\gamma$-signal in the two films (A and B) as a function of the irradiation time. After several hours of exposure, the $3\gamma$-signal decreases in both films. The dependence can be approximated by an exponential decay with different decay constants. The intensities of the $3\gamma$-signals are normalized to the respective values of these fits at $t = 0$. In order to distinguish the radiation- and vacuum-induced changes, sample A was split into two identical pieces (A1 and A2). Both specimens were placed simultaneously in vacuum, but only one (A1) was irradiated. The results from the brief measurements of sample A1 at the beginning of the irradiation and sample A2 at the end of the A1 exposure time agree within the statistical error, which rules out any detectable vacuum-related effects. (Note that these measurements had to be fast since the measurement is based on the positron beam, which is also used for the irradiation.) The initial signal increase, which occurs in sample A but not in sample B is not well understood at this time.

The spot, illuminated by the positron beam for 50 hours, can be seen in a lateral scan along the sample surface, intersecting the initial beam position. The scan of sample B, (Fig. 2) exhibits a decrease to ~0.98 in the relative $3\gamma$-intensity is seen as in Fig. 1. The full-width-at-half-maximum (FWHM) of 4.8 ± 0.2 mm was derived from a Gaussian fit (line). The FWHM is consistent with the beam cross-section of ~3.5 mm. Note that the fitted value in Fig. 2 results from the convolution of the size of the irradiated spot (equal to the beam size), and the size of the lateral scan probe (the beam). Therefore, the calculated value is 3.5 mm×√2 = 4.9 mm.

![Fig. 1](image1.png)

**Fig. 1.** The relative intensity of the 3-photon $o$-Ps decay signal in mesoporous MSSQ films (A and B). A1 and A2 are two pieces of the same sample, A2 was measured at the end of the A1 irradiation exposure to assess possible vacuum-related effects.

![Fig. 2](image2.png)

**Fig. 2.** A lateral scan of the relative intensity of the 3-photon $o$-Ps decay signal, intersecting the irradiated spot on sample B. The full-width-at-half-maximum (~4.8 mm) of the feature is consistent with the beam size (~3.5 mm).
the positron irradiation were not noticed until recently. An increasing fraction of 0-Ps in the pores undergoes annihilation of positrons, p-Ps, and pick-off insensitive to the short lifetimes originating from the thermalization process, which is nearly complete in the first 1–2% of their lifetime. Positrons spend the remainder of their lifetime either diffusing or becoming localized in the MSSQ films. The used detection scheme [7] is insensitive to the short lifetimes originating from the annihilation of positrons, p-Ps, and pick-off 0-Ps. The constant lifetime values (bottom plot) during the irradiation period show that the mean size of the pores in the film is unaffected by the irradiation. The intensity of the long lifetime decays as a consequence of the accumulated radiation dose. This indicates that with the increase of the exposure time, an increasing fraction of 0-Ps in the pores undergoes pick-off annihilation (shorter lifetime) at the expense of the characteristic ~70 ns lifetime. The intensity values are normalized as these for the 3γ-plots.

Fig. 3 shows the results from the measurements of the long 0-Ps lifetime in film B, and the equivalent pore size [8] is given on the right scale. The used detection scheme [7] is insensitive to the short lifetimes originating from the annihilation of positrons, p-Ps, and pick-off 0-Ps. The constant lifetime values (bottom plot) during the irradiation period show that the mean size of the pores in the film is unaffected by the irradiation. The intensity of the long lifetime decays as a consequence of the accumulated radiation dose. This indicates that with the increase of the exposure time, an increasing fraction of 0-Ps in the pores undergoes pick-off annihilation (shorter lifetime) at the expense of the characteristic ~70 ns lifetime. The intensity values are normalized as these for the 3γ-plots.

IV. DISCUSSION

PAS has been used in the past to study defects induced by γ, x-ray, neutron and ion radiation. However, effects due to the positron irradiation were not noticed until recently [12,13], and the technique is widely regarded as non-destructive. Typically, PAS uses 10–30 μCi radioactive β⁺ sources in bulk studies, and positron beams have intensities of 1–5 μCi. For the vast majority of the materials, the radiation dose accumulated in a measurement is insufficient to cause any measurable effects. Only a few exceptions were noted in hours-long lifetime experiments; all of them studied polymer samples.

The exceptional defect sensitivity of PAS can be utilized in early detection of radiation damage. Here, a positron beam is used to simultaneously irradiate the sample and to detect the radiation damage. The purpose of this work is to demonstrate the effects of radiation, rather than to conduct a detailed investigation of its nature, which requires more information about the material.

A. Positron and Positronium Kinetics

The accumulation of radiation damage is a kinetic process, governed by the dose rate, the bond dissociation and recombination rates, and the sample temperature. In this context, a discussion of the kinetics of the positron irradiation is helpful. Chemical bonds are broken during the positron thermalization process, which is nearly complete in the first 1–2% of their lifetime. Positrons spend the remainder of their lifetime either diffusing or becoming localized in the MSSQ films. The repulsive dipole potential at a pore surface confines the positrons to the solid, or exist as Ps. Ps can be formed in the solid, or at the pore surface, in a region limited by the positron diffusion length (20–30 nm in these MSSQ films). Subsequently, Ps may remain in the solid, or may diffuse and become localized in a pore. The Ps diffusion length in organic and inorganic polymers is ~1 nm [21]. Since only trapped in pores Ps contributes to the presented here results, the small relevant diffusion lengths are indicative of a high probability of Ps detecting a broken bond created during the thermalization of its own positron.

This scenario, however, is not sufficient to explain the monotonically decreasing intensities (Fig. 1 and 3) without the existence of an energy barrier for bond reconstruction. The low positron current density, combined with the short Ps lifetime, set a negligible probability for the coexistence of two Ps atoms at the same time. Hence, the cumulative nature of the observed effects implies that Ps detects damage caused by prior positron injection. Therefore, broken bonds cannot recombine at room temperature for times compatible with the duration of the experiments. Future studies are needed to assess the annealing behavior at a higher temperature.

B. Radiation Exposure

In thin film studies, for which positron beams are used, the induced radiation dose can exceed significantly that of a bulk source. For a reference, the β⁺ decay of 22Na has a mean energy of approximately 200 keV; these positrons penetrate a polymer sample to a 200–300 μm depth. By a comparison, a beam with a 100 times smaller energy (2 keV) penetrates to a ~100 nm mean depth. For an identical spot size (typically 3–5 mm in diameter in both cases) and similar intensity, this translates into an order of magnitude larger dose rate incurred by a positron beam exposure.

The maximum accumulated dose in these studies is many times smaller than the dose acquired in a single image obtained by a scanning electron microscope (SEM). For an order-of-magnitude estimate, consider a 100×100 μm² area of the sample, irradiated by electrons with a ~10 pA current for ~20 s. For 2 keV electrons (identical energy deposition to that of the 2 keV positrons), the dose rate is 10⁸ times greater (10⁷ times larger current; 10⁵ times smaller volume), while the exposure time is 10⁶ times shorter. For this example, the dose by an SEM is some 100 times larger than that of the maximum achieved dose in these experiments.
C. Damage Detection

The signature of $\alpha$-Ps annihilating in the pores provided the most conclusive confirmation of the radiation damage. The separation of this signal from the annihilation of positrons, $p$-Ps and pick-off $\alpha$-Ps is straightforward for materials with nanometer-sized pores. The $3\gamma$ $\alpha$-Ps self-annihilation measured prior at the beginning of the experiments (at a negligible radiation dose) was $-46\%$ for sample A, and $-34\%$ for sample B, whereas the contribution from the MSSQ matrix was only $2\%-3\%$. The normalized intensity in Fig. 1 ignores these material-related differences. The separation of the $70\,\text{ns}$ $\alpha$-Ps lifetime from the other lifetimes is also trivial [7]. Thus, the shown results are representative of the electronic environment at the pore walls, which is probed by the trapped in the pores $\alpha$-Ps. Radiation damage, which occurs in the MSSQ matrix, is not evident from these data, but it is implied by virtue of the identical bond configuration in the bulk.

The evidence relating the positron beam with the radiation damage is contained in Fig. 1 and 2. The results from the measurements of A1 and A2 at $t = 0$ (Fig. 1) rule out any film changes, which could be associated with the transition from air to vacuum, or attributed to a prolonged vacuum exposure. Further confirmation is obtained from Fig. 2, where the irradiated spot is cross-sectioned, and its FWHM is consistent with the beam size.

Structural changes in the films are ruled out by the results in Fig. 3. The long $\alpha$-Ps lifetime (bottom), which remains constant throughout the duration of the experiment, rejects changes in film thickness due to a gradual decrease in the pore size. Further, optical observations rule out a $-30\%$ change in film thickness, which would be implied by the decreased intensity (top), if interpreted as a sign of collapsing pores. Therefore, we conclude that the mechanical structure of the films and the morphology of the porosity remain unchanged.

We attribute the radiation damage to broken bonds near the pore walls. This changes the electronic environment, leading to enhanced pick-off annihilation. The mechanism of this enhanced pick-off process can be Ps interaction with paramagnetic centers [17], or a chemical interaction [18]. In the former case, $\alpha$-Ps undergoes a spin-flip due to the mixing of the $(0,0)$ $p$-Ps and $(1,0)\alpha$-Ps states, and subsequently annihilates with the characteristic fast rate of the $\uparrow\downarrow$ spin configuration. In the latter case, Ps (like hydrogen) binds to dangling bonds or free radicals, and is unable to probe the open volume of the pore. The increased electron density at the wall enhances the probability for pick-off annihilation.

D. Relevance to Space Environments

The use of low-$k$ COTS microcircuits in space applications will require assessment of their performance under electron, proton, and heavy ion radiation. The present results relate to electron radiation by virtue of the similarity of electron and positron ionization for energies greater than $1\,\text{keV}$. High-energy electrons, which slow down to $-\text{keV}$ energies in the dielectric of a low-$k$ COTS device, will cause similar damage as $-\text{keV}$ electrons injected in a bare MSSQ film. Qualitatively similar damage can be created by other ionizing radiation.

The emphasis of this work was not on the positron-induced radiation damage, but rather on the detection method for broken bonds. Quantitative investigations of radiation effects in low-$k$ materials require the use of radiation standards, such as $x$-rays and $\gamma$ sources, and high-energy particle beams as in device tests. For that, PAS can be utilized in the detection of radiation damage in a material at low doses. The benefit of using Ps as a probe is in its sensitivity to the local electronic environment at the pore surface, and its strong interaction with unsaturated bonds. Using PAS in the prescribed way will enable the search for correlation between materials properties and device performance. In a plausible scenario, the dielectric properties of the media can be altered due to the change in the polarization as a consequence of creating broken bonds or free radicals. This can affect the signal propagation delay, which, in turn, can alter the timing response of a device.

The accumulation of broken bonds in a low-$k$ polymer ILD raises new concerns for using such microcircuits in space radiation environments. Cross-linking of a MSSQ low-$k$ dielectric has been achieved by using electron beams as an alternative to thermal curing [22]. Bond rearrangement under electron irradiation increases the polymerization degree, and the films become harder and more brittle. The polymerization of a low-$k$ ILD must be balanced between achieving sufficient hardness, needed to comply with the mechanical requirements of a package, without becoming brittle, which can make them susceptible to fracture under residual stresses. In an earth-like environment, the radiation dose to a low-$k$ material, accumulated during electron-beam cross-linking or other fabrication steps, will practically seize to increase in a finished product. In radiation environments, however, the degree of polymerization, and thereby the ILD’s hardness, can increase continuously.

The emergence of state-of-the-art low-$k$ devices, such as ASICs, SRAMs, etc., can be used to enhance the capabilities of space missions. However, the lack of relevant information at the present hampers the evaluation of their performance.

V. CONCLUSIONS

We demonstrated radiation-induced degradation of low-$k$ methyl-silsesquioxane, which is a promising candidate to replace silica as interlayer dielectric in advanced integrated microelectronic circuits. The samples were irradiated by $2\,\text{keV}$ positrons, which create similar damage to that of $2\,\text{keV}$ electrons. The high sensitivity of a positronium atom ($e^-\text{e}^-$) to unpaired electrons (e.g., broken bonds or radicals) was used to detect the damage at low doses. This establishes the feasibility of using positron annihilation spectroscopy as a characterization tool for the assessment of material damage induced by photon ($x$-ray, $\gamma$), electron, proton, or ion radiation.

Some issues, concerning the utilization of low-$k$ electronic components in satellites and spacecrafts, are discussed. These polymers can be susceptible to changes in their electrical and mechanical properties, which can lead to new failure modes. It must be stressed, however, that little information exists about the performance of this new class of materials beyond the specifications for commercial grade electronics. Future investigations are warranted.
ACKNOWLEDGMENTS

The work described in this paper was performed at the Washington State University, sponsored by the U.S. National Institute of Standards and Technology (NIST/ATP Cooperative Agreement No. 70NANB8H4013). The writing and publication of this paper was supported by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

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