

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

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Abstract

Low-*k* methyl-silsesquioxane films were irradiated by a 2 keV low-current (~30 fA) positron beam. Bond-breaking was observed at <1 Gy cumulative doses, implying more significant effects upon electron irradiation in space or by electron microscope.

SUMMARY

Introduction

At present times, performance improvements in state-of-the-art microelectronic devices can no longer be achieved mainly through miniaturization of 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) interlayer dielectrics (ILD), metal diffusion barriers, high- k materials for capacitors and gate dielectrics, etc. [1]. The quest for the successful low- k ILD-candidate has focused mainly on polymer families (organic, inorganic, and their hybrids), CVD, and sol-gel materials, which can incorporate embedded porosity to achieve further decrease in k . However, the knowledge of their physical and electronic properties is limited, and the lack of relevant data renders the evaluation of their performance in radiation environments highly speculative. A merit of the importance of such evaluations is the increasing tendency of using commercial off-the-shelf (COTS) parts in satellite and spacecraft systems.

Some materials properties can be critical for the performance of integrated circuits in high radiation environment, regardless of the circuit architecture. Thus it is important to assess their behavior independently. For this end, we studied blanket methyl-silsesquioxane (MSSQ) films, which are promising ILD candidates with high commercialization potential.

Experiment

Thin ($\sim 0.7 \mu\text{m}$) mesoporous MSSQ films were fabricated by the sacrificial porogen technique [2]. Si wafers were spin-coated with a solution containing low molecular weight MSSQ resin and volatile polymer additive (pore generator, or porogen). The samples were treated thermally in steps first (at $200 \text{ }^\circ\text{C}$) to vitrify the MSSQ without affecting the porogen, and then (at $450 \text{ }^\circ\text{C}$) to decompose the porogen, which leaves behind voids embedded in the MSSQ network. The studied samples, designated as A and B, contained approximately equal porosity fraction ($\sim 20\%$), but were produced using different MSSQ resins and porogens.

A monoenergetic low-current ($\sim 30 \text{ fA}$) positron beam was used to simultaneously irradiate the samples and to probe the porosity for up to 50 hours. Thermalized and low-energy ($\sim 1 \text{ eV}$) positrons in insulators can bind with electrons to form positronium (Ps – a light analog of atomic hydrogen), which forms (as hydrogen) in two spin states – *para* (singlet) and *ortho* (*o*-Ps, triplet). The *o*-Ps is a unique characterization probe for large ($>1 \text{ nm}$) pores; its lifetime is a measure of the pore size [3-5], and its decay mechanism (via 2- or 3-photons) yields open porosity fraction and pore connectivity [6,7]. Here, the long *o*-Ps lifetime and the 3-photon (3γ) *o*-Ps decay in the middle of the film (2 keV incident beam energy) were monitored as a function of the irradiation time.

Results

Figure 1 shows the 3γ -signal in the two films (A and B) as a function of the irradiation time. After several hours of exposure, the 3γ -signal decreases in both films. The dependence can be approximated by an exponential decay with different decay constants. The intensities of the 3γ -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 pieces 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.

Figure 2 shows changes in the relative 3γ -intensity in a lateral scan of sample B, intersecting the spot where the positron illuminated the sample for ~ 50 hours. The position of the irradiated spot is seen clearly, and its full-width-at-half-maximum of 4.8 ± 0.2 mm is consistent with the measured beam cross-section of ~ 3.5 mm ($3.5 \text{ mm} \times \sqrt{2} = 4.9 \text{ mm}$).

Figure 3 depicts the results from measurements of the long o -Ps lifetime (as in Ref. [8]) in film B, and the equivalent pore size (right scale). 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 this lifetime, however, decays as seen in the 3γ -measurements, and indicate a decrease in the number of pores detected by the Ps probe. The intensity values are normalized as these for the 3γ -plots.

Discussion

Polymer degradation of polymers after irradiation by a bulk positron source is known. A positron spectrum from a bulk radioactive source has a broad energy distribution with a mean energy of the order of 100 keV. Their typical penetration depth in materials, within which their initial energy is deposited, is ~ 0.1 mm. Monoenergetic positron beams can deposit similar energy density at incident energies of ~ 1 keV. Despite their $\sim 10^2$ lower energy and $\sim 10^3$ times smaller typical intensity compared to bulk sources, which combine for a $\sim 10^5$ times lower power, the volume in which the energy is deposited can also be 10^5 times smaller. To our knowledge, a positron beam-induced polymer damage has not been seen previously.

The shown results characterize o -Ps annihilation in the pores of the films. (The o -Ps annihilation in the MSSQ network can be ignored, as its lifetime is 3-3.5 ns [9], and its 3γ annihilation signal is $\sim 2\%$ [10], as opposed to 35-40% in these porous films). It is evident that the mean pore size remains unchanged during the irradiation (Figure 3, bottom), which rules out film shrinking. Therefore, we conclude that the mechanical structure of the films and the porosity morphology remain unchanged after small dose of radiation (< 1 Gy in these experiments).

We attribute the suppression of the long o -Ps lifetime component to the appearance of broken bonds at the surface of the pores, which changes the local electronic environment. Being chemically similar to hydrogen, Ps is attracted and binds to unsaturated bonds. There the electron density is high, and therefore the lifetime is short (typically a few ns). Furthermore, kept at the pore wall in proximity to molecular electrons, the 2γ annihilation is dominant. The signatures of such o -Ps annihilation do not contribute the shown lifetime and 3γ data, but cause the observed signal suppression.

Positron radiation is not a concern for space missions. It should be stressed, however, that for energies greater than 1 keV positron and electron radiations cause similar effects in matter. 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. The present results relate directly to electrons, and the observed bond-breaking at such small doses (< 1 Gy) raises serious concerns. The creation of unsaturated bonds in polymers increases the degree of polymerization,

which governs the film's mechanical properties. The polymerization of low-k ILDs must be balanced: less cross-linked films are soft, while more cross-linked films become brittle. Therefore, devices using ILD polymers may be susceptible to failures caused by fracture formations.

Conclusions

We demonstrated degradation of low-k MSSQ films, polymer ILD-candidate material, induced by small-dose (<1 Gy) irradiation by low-energy (2 keV) positrons. The results imply that similar processes should occur in electron irradiation environments, such as these in space or in electron-based materials characterization tools. This raises a concern for future state-of-the-art electronics used in satellites and spacecrafts, whose low-k dielectrics may be susceptible to crack formation, which may lead to device failures. Future quantitative investigation is warranted.

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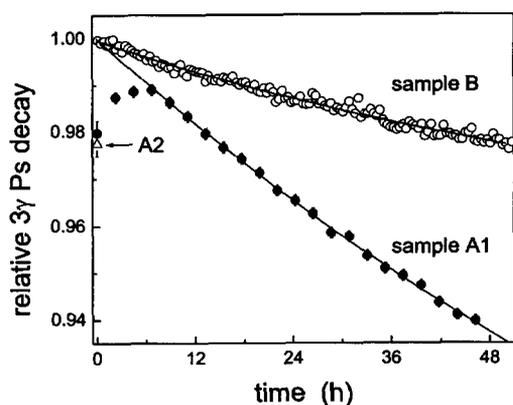


Figure 1. The relative intensity of the 3-photon *o*-Ps decay signal in mesoporous MSSQ films (A and B). A1 and A2 are two pieces of the same sample; A2 was measured at the end of the A1 irradiation exposure to assess possible vacuum-related effects.

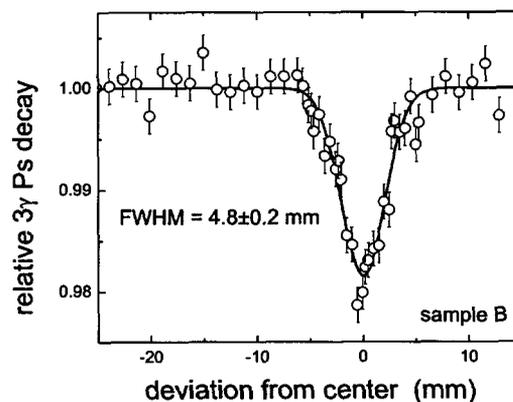


Figure 2. A lateral scan of the relative intensity of the 3-photon *o*-Ps decay signal, intersecting the irradiated spot on sample B.

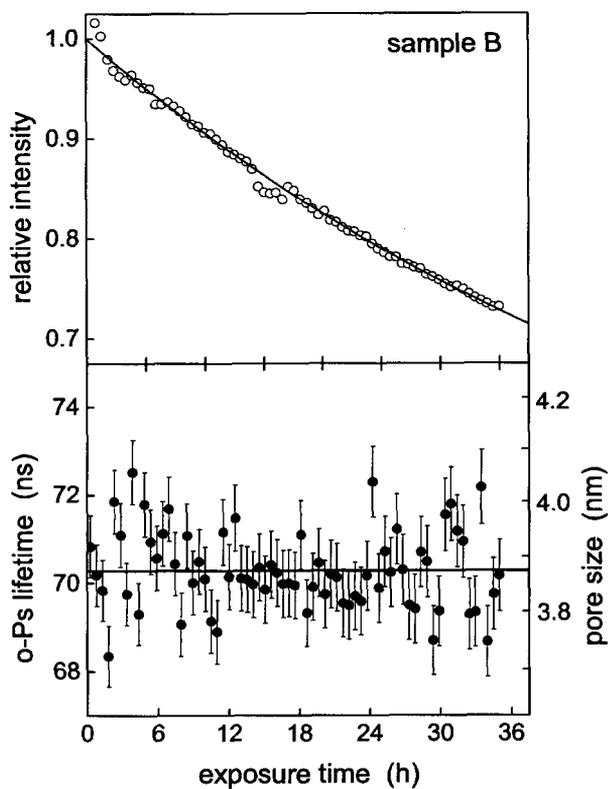


Figure 3. Top: The relative intensity of the long *o*-Ps lifetime in sample B, measuring the density of pores, whose electronic environment remains unaffected by the positron irradiation.

Bottom: The *o*-Ps lifetime as a function of the irradiation time remains unchanged, ruling out changes in the mean pore size.