Radiation-Induced Charge Trapping in Low-k Silsesquioxane-Based Intermetal Dielectric Films

R. A. B. Devine, J. W. Tringe, and J. R. Chavez

Abstract—**Radiation-induced charge trapping has been studied in cured hydrogen silsesquioxane low dielectric constant films subjected to electric fields during the radiation process. Evidence is found for electric field-dependent negative charge trapping with a dose$^{0.47}$ variation. The possible origin of the negative charge trapping is discussed.**

Index Terms—**Low-k dielectric, radiation effects, silsesquioxane, thin film, X-ray.**

I. Introduction

The low-frequency dielectric constant of amorphous SiO_2 used traditionally as an intermetal insulator in silicon microelectronics circuits is 3.9. It is now well established [1] that this value is too high for future generations of circuits where resistance/capacitance delay of the interconnect lines will dominate the switching speed of circuits. In consequence, there is substantial activity with commercial circuit manufacturers to develop alternative dielectrics with relative permittivities as low as possible. Two major physical constraints concern the adhesion of the interconnect metal to the chosen dielectric and the mechanical strength of the material when such processes as chemical–mechanical polishing are used in planarization. In the medium term, it would appear that SiO_2-based material solutions are viable, although the dielectric constant is reduced, typically, to only $\sim$2.9.

One choice of material is a flowable oxide (FOx) developed by Dow Corning. This dielectric is based on hydrogen silsesquioxane (HSQ) and has a molecular structure $(HSiO_{3/2})_{2n}$ with $n = 2, 3, 4\ldots$. The typical cage-like molecular structure for $n = 4$ is shown in Fig. 1(a). Immediately obvious is the large open volume that results in a low molar polarizability per unit volume and, hence, lower dielectric constant. HSQ films are obtained by spinning on HSQ dissolved in a solvent and then curing; the resinous form of HSQ is shown schematically in Fig. 1(b). One observes that curing results in opening and cross-linking of cages to form an extended, three-dimensional network [2]. We note that the cross-linking takes place in such a way that a "pure" SiO_2 network is not formed and some structural defects such as $HO_2 \equiv Si–Si \equiv O_2H$ are naturally present—two examples of these are shown in Fig. 1(b). This defect is similar to the neutral oxygen vacancy, which is known to be a hole trap. The question that now arises is: if these materials are to be used in circuits, which may find their way into space or other hostile environments, will they be particularly radiation sensitive, and will this therefore be deleterious to their incorporation?

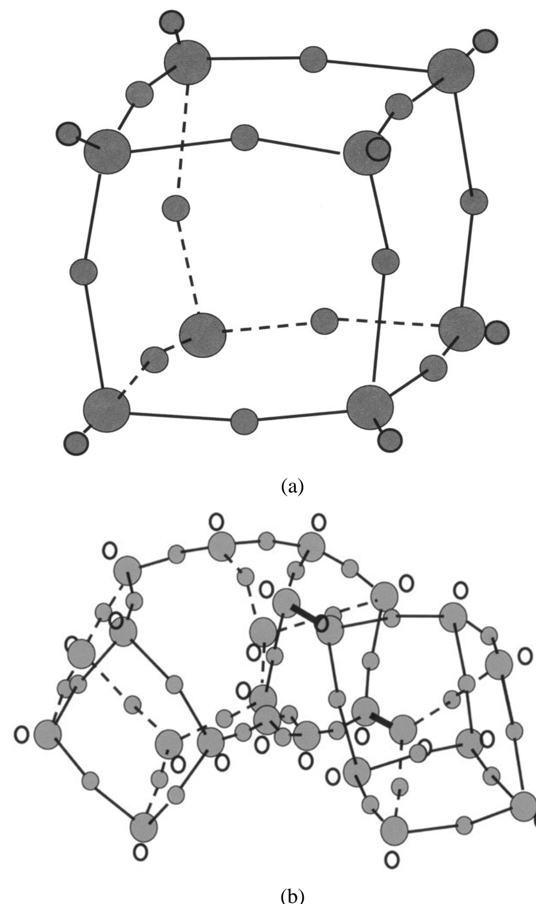

Fig. 1. (a) Atomic representation of a basic cage and resinous structure of HSQ. Large atoms = Si, smaller gray atoms = O, small open circles = H. (a) HSQ cage for $n = 4$. (b) Resinous form of HSQ shows cross-linking of cages. The thick lines linking two Si atoms in the center of the diagram indicate neutral oxygen vacancy sites.

In the following, we report the preliminary results obtained from a study of the X-irradiation sensitivity of one low-k dielectric, FOx 12. We underline from the outset that because these materials are very fragile, it is extremely difficult to obtain ideally reproducible data. For these reasons, although the scatter in data is not as limited as we would have hoped, we can obtain some first indication of the radiation sensitivity of HSQ.

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14. ABSTRACT

Radiation-induced charge trapping has been studied in cured hydrogen silsesquioxane low dielectric constant films subjected to electric fields during the radiation process. Evidence is found for electric field-dependent negative charge trapping with a dose {sup 0.47} variation. The possible origin of the negative charge trapping is discussed.

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II. Experimental Details

FOx 12 HSQ methyl isobutyl ketone solution was obtained from Dow Corning. The solution was spun onto 4″ Si p type epi-wafers at 2000 rpm and then subjected to a sequence of curing steps recommended by Dow Corning, terminating with a one-hour cure at 400 °C in flowing N_2. Prior to spinning, the wafers were subjected to a 50% HF acid drip and blown dry. The film thickness so obtained was ~115 nm with a refractive index ~ 1.38 ($\lambda = 632.8$ nm). The back face of the wafer was then metallized with Al in a thermal evaporator and a series of Al capacitor dots produced on the HSQ film using a shadow mask. The Al thickness was typically >500 nm, and this was crucial to minimize piercing or stressing of the HSQ film by the tungsten probe used to contact the Al dot. No post-metallization anneal in forming gas was performed. The physical properties of the films produced in our facility were consistent with those quoted by Dow Corning and measured on samples provided to us by them.

The material was characterized by measuring the capacitance/voltage curves $[C(V)]$ at 100 kHz and using them to ascertain the flat-band voltage [3]. As a general rule, we measured flat-band voltage shifts of the $C(V)$ curves from their initial conditioned but unirradiated positions. Because the curve shape was found to displace but not to deform as a function of irradiation, this procedure was considered acceptable and negated the necessity to include interface state density effects. Note that because the samples were not forming gas annealed, the density of states at the HSQ/Si substrate interface was typically ~7×10^{11} states eV^{-1} cm^{-2} [4]. Irradiations were carried out using an ARACOR system with a tungsten target. The accelerating voltage was 50 kV, and the typical dose rate was ~157 rad (Si) per second. Total doses up to 1000 krad (Si) were accumulated. Irradiations were carried out with applied electric fields of ± 1 MV cm^{-1} and -0.5 MV cm^{-1}. Because of the charging characteristics of the HSQ material, a series of preconditioning steps was necessary prior to irradiation in certain cases. These will be detailed in the following section.

III. Results

We have demonstrated previously that as-made HSQ films contain mobile positive and negative charges [4]. The mobile negative charges (which we assume are electrons) can be removed rapidly from the HSQ films by application of a modest electric field (~± 1 MV cm^{-1}). Experiments under positive and negative bias demonstrate that the positive charge (which may be holes or charged ionic species) is not removed from the HSQ film but is simply electric field drifted. If the charge is drifted to one interface of the film (metal/HSQ or substrate/HSQ), it will subsequently drift back if left in an unbiased mode [4]. This means that even if we polarize the samples prior to irradiation to drive the positive charge to one of the interfaces, irradiation experiments in an unbiased mode are not feasible. Therefore, all our irradiations were carried out in a biased mode, in this case, with an applied electric field of -1 MV cm^{-1}, -0.5 MV cm^{-1}, or $+1$ MV cm^{-1}.

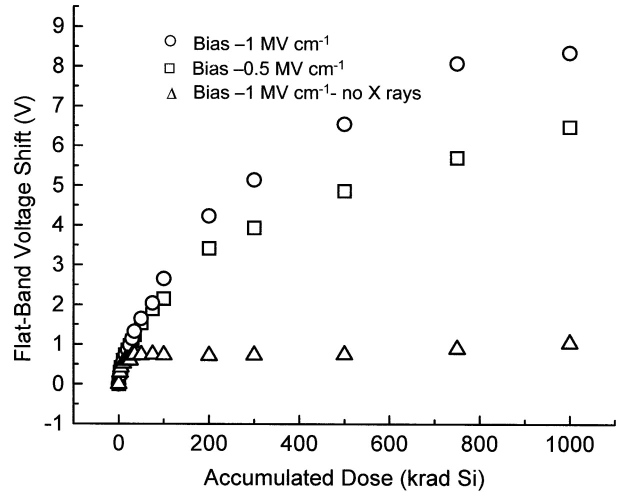


Fig. 2. X-ray dose-dependent variation of the flat-band voltage from the preconditioned value in three configurations: (○) bias field -1 MV cm^{-1} during irradiation; (□) bias field -0.5 MV cm^{-1} during irradiation; (△) bias field -1 MV cm^{-1} for same irradiation time but no X-rays.

For the case of negative applied fields during irradiation, preconditioning involved applying a field of -2 MV cm^{-1} for periods from 60 to 90 minutes. This was sufficient to drive the mobile positive charges to the metal gate/HSQ interface and, it was hoped, for the bias during irradiation to hold them there during irradiation. Because the substrates used for the experiments were p-type, the $C(V)$ curves were measured by sweeping typically from -20 V to 0 V in 20 seconds. This sweep range also helped to maintain the mobile positive charge at the Al/HSQ interface. However, as we shall see, there is evidence that even with these precautions, charge motion during the time of irradiation occurred. The flat-band voltage prior to irradiation (following preconditioning) was ascertained, and the flat band voltage shift as a function of radiation dose up to 1000 krad (Si) under bias was then measured. In Fig. 2, we show the flat-band voltage shift: $\Delta V_{FB} = V_{FB}(\text{dose}) - V_{FB}$ (pre-conditioned) for the two applied fields used in the negative bias experiment.

We also include in the figure data for samples subjected to the measurement steps and bias voltages appropriate for each irradiation time but without the presence of the radiation. For a constant dose rate of radiation, accumulated dose corresponds essentially to time. Consequently, although one set of samples (open triangles) received no exposure, we can compare the flat band voltage shifts in the irradiated and unirradiated samples and conjecture what part of it is simply due to the effects of time and bias voltage. By subtraction, one can obtain the effective flat-band voltage shift variation due only to the effects of radiation; this is plotted in Fig. 3 for both negative bias fields. It is clear from the unirradiated data shown in Fig. 2 that some component of the flat-band voltage shift existed due to mobile charge motion during the time necessary for the radiation experiment.

The situation for the case of positive bias during irradiation was exacerbated because although positive bias was used to precondition the mobile charge ($+2$ MV cm^{-1} for 60 to 90 minutes), the $C(V)$ was obtained by sweeping from -20 V to 0 V.

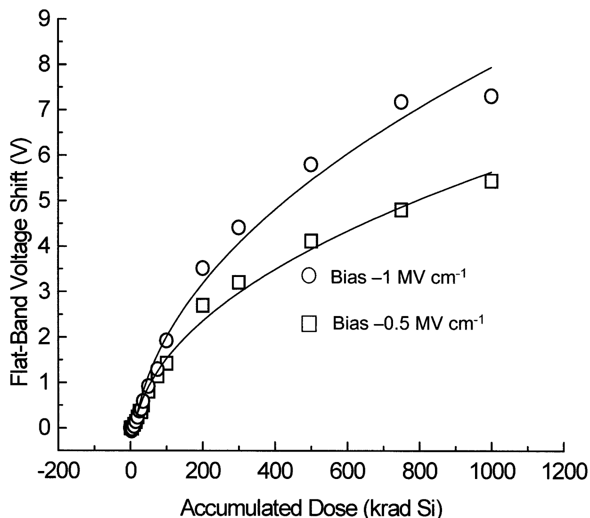


Fig. 3. Data from Fig. 2 after subtraction of effect of evolution of the distribution of the mobile charge distribution during the time of exposure to X-rays and during the $C(V)$ curve sweep time. The solid lines show a power law curve fit assuming $\Delta V_{FB} = a(\text{dose})^b$.

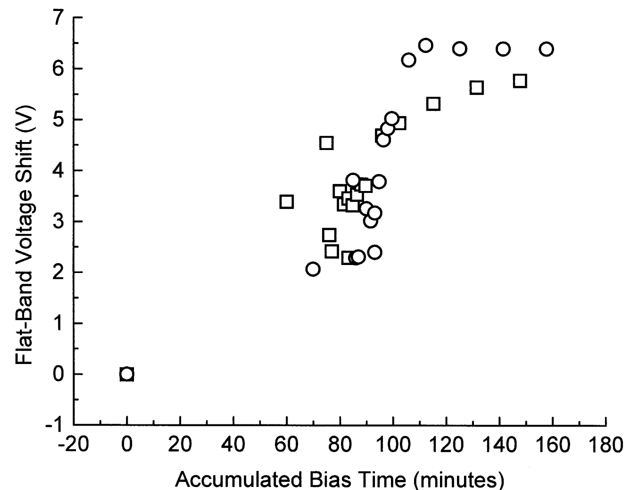


Fig. 4. (□) Accumulated bias time dependence of the flat-band voltage shift for samples exposed in the presence of a $+1$-MV cm^{-1} electric field and a dose rate of 157 rad (Si) s^{-1}. (○) samples subjected to the same bias field for the same time as the irradiated samples not exposed to the X-rays.

In consequence, charge motion was expected and observed. Following the procedure used for the case of negative fields, we obtained data on unirradiated and irradiated samples subjected to the same time/bias stressing. Typical data for unirradiated and irradiated samples subjected to a bias field of $+1$ MV cm^{-1} is shown in Fig. 4. Note that the x-axis is the accumulated bias time. In order to calculate the dose received by the irradiated sample, one simply multiplies this time by the dose rate [157 rad(Si) per second]. Although there is significant scatter due, we assume, to mobile charge motion during measurement and biasing, we can conclude that there is negligible charge trapping-induced flat-band voltage variation resulting from the radiation in the presence of the positive electric field.

IV. Discussion

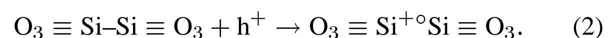
The data presented in Fig. 3 clearly evidence the trapping of radiation-induced negative charge. Although the flat-band voltage in the conditioned, unirradiated samples was ~ -4 V, the flat-band voltage shift shown in Fig. 3 exceeds $+7$ V for a dose of 1000 krad (Si). The flat-band voltage is written [3]

$$V_{FB} = \phi_{ms} - Q_f / C_{ox}, \tag{1}$$

where Q_f is the trapped oxide charge and C_{ox} is the oxide capacitance. ϕ_{ms} is the work function difference between the gate electrode material (Al) and the semiconductor substrate. For our case, we estimate $\phi_{ms} \sim -0.8$ V. The flat-band voltage shift, ΔV_{FB}, induced by negative charge trapping then corresponds to a total trapped charge (negative) density $\sim 9 \times 10^{11}$cm^{-2} for a dose of 1000 krad (Si) in the sample subjected to a field of -1 MV cm^{-1} during irradiation. A simple fit to the experimental data, shown by the solid lines in Fig. 3, suggests that $\Delta V_{FB} = a(\text{dose})^b$ with $b = 0.47$ for the case of irradiation in the presence of a -1-MV cm^{-1} electric field and $b = 0.45$ for the -0.5-MV cm^{-1} case. We attach no particular significance to these numbers other than to note that a power law dependence of ΔV_{FB} is also common [5], [6] for amorphous SiO_2.

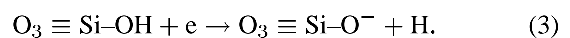
The data shown in Fig. 4 for positive polarization during irradiation suggests that there is no measurable charge trapping in this mode or at least the flat-band voltage shift for a dose of 1000 krad (Si) at $+1$ MV cm^{-1} is $< +1$ V. Note that positive bias should sweep the negative charge (which generates positive flat-band voltage shifts) to the gate electrode, where it would have no influence on the flat-band voltage [3]. Such a polarization would, however, drive positive charge to the HSQ/substrate interface where it should have some influence in driving the flat-band voltage more negative. The data in Fig. 4 suggest that if there is any radiation-induced shift, it is positive, consistent with negative charge trapping. The dominant mechanism of charge trapping in these materials appears, then, to be associated with negative charge (electrons).

Although the structure of HSQ shown in Fig. 1 is expected to be significantly different from amorphous SiO_2, it is interesting to compare their properties under irradiation. In thermally grown, amorphous SiO_2, the radiation-induced charge trapping usually involves positive charge [5] and the trapping site is assumed to be a neutral oxygen vacancy center



$$O_3 \equiv \text{Si–Si} \equiv O_3 + h^+ \rightarrow O_3 \equiv \text{Si}^{+\circ}\text{Si} \equiv O_3. \tag{2}$$

Significant negative charge trapping in dry, amorphous SiO_2 is unusual unless the oxide has been subjected to extended thermal anneals at high temperatures. Negative charge trapping in wet oxides has been suggested [7] to be associated with electrons trapped at dangling Si–O bonds resulting from the release of hydrogen from Si–OH terminations



$$O_3 \equiv \text{Si–OH} + e \rightarrow O_3 \equiv \text{Si–O}^- + \text{H}. \tag{3}$$

However, the capture probability of an electron in a wet oxide is estimated to be 10^{-3} smaller than for a hole in a dry oxide [5] so that in general one expects (and observes) hole trapping to dominate in irradiated oxides essentially independent of the nature of the oxide (wet or dry).

The observation of dominant electron trapping and no significant hole trapping in HSQ films is surprising. However, given

the nature of the molecular bonding in HSQ (significant quantities of H), it would not be unusual to find substantial densities of Si–OH terminations in the cured material so that a negative charge trapping mechanism such as (3) would be important. Somewhat more unusual when one considers Fig. 1(b) is the apparent absence of sizable positive charge trapping. It is suggested that the cage-like structure develops into a three-dimensional network and periodically forms Si–Si linkages (neutral oxygen vacancies), which help the linking [see, for example, Fig. 1(b)]. From (2), we would expect these sites to be hole traps, but clearly this is either not the case in HSQ or the numbers of such sites is in fact limited.

V. Conclusion

Preliminary measurements of radiation-induced charge trapping in low-temperature cured HSQ films have been made using the $C(V)$ technique. The measurements are complicated by the presence of existing, mobile positive charge in the as-made films; these charges clearly move during the measurement process. Despite these difficulties, we have clearly demonstrated substantial negative charge trapping in samples subjected to negative electric fields during the irradiation, which has a power law variation with dose. The charge trapping is field dependent. We suggest that it may be related to a high density of Si–OH dangling bonds present in the cured films.

The question, which remains, is whether these materials would be troublesome in space applications. At first sight, it would appear that they would be no more hazardous than if amorphous SiO_2 were used, at least in terms of the risks of charge generation and trapping. Because the materials would presumably not contact the Si substrate surface (for example, they would not be used as field oxides), charging is not likely to be a potential problem at first sight. Still to be ascertained, however, is whether the radiation modifies their electrical conductivities and enhances breakdown—this could be problematical.

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