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# One Gigarad Passivating Nitrided Oxides for 100% Internal Quantum Efficiency Silicon Photodiodes

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*Abstract*

100% internal quantum efficiency silicon photodiodes with 4 to 8 nm passivating silicon dioxide have been fabricated by rapid thermal nitridation in nitrous oxide and ammonia ambients with the aim of increasing their radiation hardness. The fabricated diodes were exposed to 10.2 eV photons using a hydrogen plasma light source and a normal incidence monochromator. The measured quantum efficiency degradation indicates that the interface trap area density ($N_{it}$) increases sublinearly with dose up to a measured dose of one Gigarad. No noticeable change in quantum efficiency over the range of 50 to 250 nm was observed after exposure to 100% relative humidity. This suggests that the nitrided Si-$SiO_2$ interface is practically insensitive to moisture.

## I. INTRODUCTION

Research in the spectral region encompassing the vacuum ultraviolet, extreme ultraviolet, and soft X-rays (here referred to as the XUV, with photon energies from 6 to 6000 eV) is currently very active, due to the importance in X-ray lithography, X-ray microscopy, plasma diagnostics, and space and basic scientific research [1]. In spite of an obvious need in the above scientific disciplines, no reliable detector for the full XUV exists. The main obstacle in fabricating a good silicon XUV detector has been the presence of a 'dead region' near the surface, formed during the fabrication process. Due to the extremely short absorption depths of XUV photons in silicon, this "dead region" will absorb most of the photogenerated carriers. The loss of photogenerated carriers will result in unacceptably low quantum efficiencies. The problem of realizing a good XUV silicon photodiode was further exacerbated by the relatively poor quality of the surface passivating $SiO_2$. Since this is effectively an entrance window for photons, interaction with XUV photons would tend to degrade device efficiencies.

Fabrication of a silicon p-n junction without creation of a surface 'dead region' (no recombination of photogenerated carriers in the doped $n^+$ region, or at the Si-$SiO_2$ interface) was reported recently [2,3]. Subsequently, it was shown that these diodes do exhibit near-theoretical quantum efficiencies for XUV photons when their passivating $SiO_2$ layer was reduced to 4-8 nm in thickness [1,4]. However, the radiation hardness (as evidenced by radiation-induced change in the quantum efficiency of less that 4%) at 10.2 eV photon energy was only 50 Mrad[1]. This was felt to be unacceptably low for radiometric applications, in which detector degradation should be minimized. As the diodes have (pre-exposure) zero surface recombination [5,6], it is assumed that the change in the quantum efficiency occurs due to surface recombination caused by an increased number of radiation-induced interface traps. This work describes fabrication and characterization of 100% internal quantum efficiency diodes with 4–8 nm passivating nitrided $SiO_2$, which have exhibited radiation hardness of 1 Gigarad for 10.2 eV photons.

## II. EXPERIMENTAL

Figure 1 shows a schematic of the 100% internal quantum efficiency photodiode, which has 1 $cm^2$ active area, and is fabricated on 100 mm diameter, p-p+ wafers with a 10 µm thick, 5 ohm-cm epitaxial layer. After the standard $p^+$ channel stop and $n^+$ guard ring diffusions, phosphorus diffusion was carried out to achieve zero surface recombination without a diffused "dead region"" [3]. The passivating 4–8 nm thick $SiO_2$ layer was grown in a mixture of nitrogen and oxygen ambient at 900 °C using a super dry oxidation process similar to one reported in Ref. 7. Wafers with this ultra-thin dry oxide were subjected to rapid thermal nitridation at 1065–1165 °C for 45 seconds in ammonia and nitrous oxide ambients. Wafers nitrided in ammonia were also subjected to a short reoxidation treatment to remove the hydrogen from the film. Wafer heating and cooling rates of 5 to 25 °C/s were adopted. The nitridation was performed in a Peak Systems

[1] The absorbing material for all radiation doses cited throughout this paper is silicon dioxide.

Model 5500 rapid thermal processor[2]. Subsequent processing involved masking, aluminum metalization, post-metal anneal, Cr-Au deposition at the rear, and sawing. More details on the diode fabrication process are available in Refs. 1 and 3.

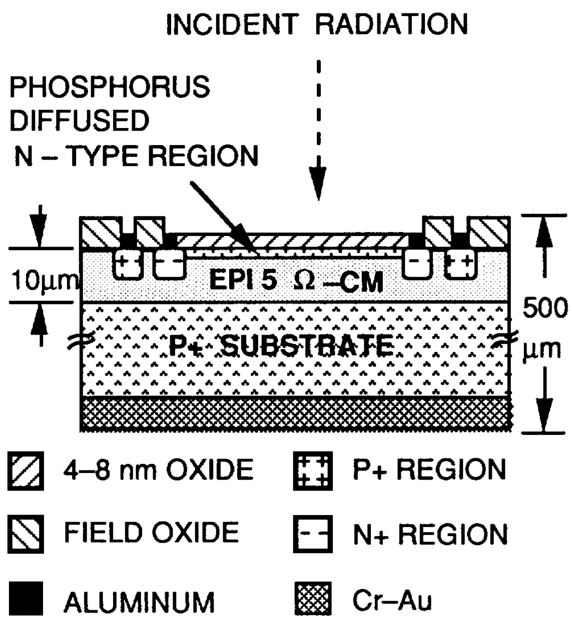


Fig. 1 Schematic of the silicon photodiode investigated.

The fabricated chips were assembled in a two-lead ceramic package. Radiation testing was performed at 10.2 eV because of the extremely high oxide absorption at this photon energy (1/e absorption length of <10 nm [8]), yielding a high radiation dose in a relatively short time. Additionally, these XUV photons will be more useful for radiation damage studies than the higher energy photons because they create electron-hole pairs in the oxide without creating displacement damage [9].

Sensitivity and stability measurements in this work were made in the far ultraviolet detector standards calibration facilities at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. The essential details of the NIST far ultraviolet detector program have been published [10]. Spectral coverage is available over the range of 5–254 nm wavelength (248–4.9 eV photon energy), and the experimental systems enable the determination of absolute quantum efficiencies of detector samples in this spectral region. Uncertainties in the radiometric scale used to determine efficiency measurements in these system are:

| Photon Energy (eV) | Uncertainty (1 Standard Deviation (%)) |
|---|---|
| 124 | 15 |
| 10.2 | 9 |

These uncertainties would also apply to the determination of fluence (radiant flux times time), since the magnitude of the radiant flux is determined by periodic reference to a calibrated detector standard. However, relative measurements of the behavior of a sample photodiode under long-term exposure would have a much lower uncertainty, typically 1–2% (one standard deviation).

## III. RESULTS AND DISCUSSION

Figure 2 is a plot of the effect of XUV photon exposure on the efficiency of diodes with three different silicon dioxide coatings. Curve 'a' is for a diode whose $SiO_2$ was nitrided in pure $N_2O$ at 1065 °C. The thickness of the nitrided oxide was 5 nm, and this was found to be the most stable measured. Curve 'b' is for a diode nitrided in ammonia and reoxidized. The diode represented by curve 'c' did not undergo any nitridation processing.

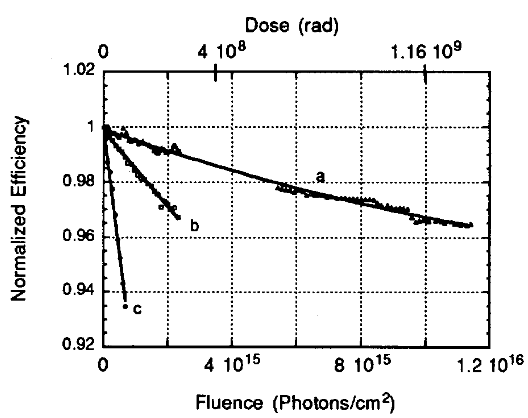


Fig. 2 Efficiency of three silicon photodiodes as a function of fluence (or equivalent dose) at 10.2 eV photon energy: without nitridation (c), and with ammonia (b), and nitrous oxide (a) nitridation . Experimental data points are shown, with least-squares fitted linear (b and c) and polynomial (a) curves.

[2] Commercial products -- materials and instruments -- are identified in this document for the sole purpose of adequately describing experimental or test procedures. In no event does such identification imply recommendation or endorsement by the National Institute of Standards and Technology of a particular product; nor does it imply that a named material or instrument is necessarily the best available for the purpose it serves.

Our results confirm the findings of other investigators [11] that devices nitrided in $N_2O$ have superior hardness that devices nitrided in $NH_3$. Diodes nitrided in the $N_2O/O_2$ ambient exhibited lower radiation hardness presumably owing to the lower nitrogen incorporation in the Si-$SiO_2$ interface [12].

The improvement in radiation hardness with an increasing degree of nitridation can be explained using the bond strain gradient model proposed by Grunthaner *et al.* [13]. This model indicates that the interface states are caused by migration of radiation-induced defects within the strained region toward the Si-$SiO_2$ interface, with the strain acting as the driving force. Thus, the amount of interface state generation depends on the degree of strain at the interfacial region and also on the distance in the oxide over which the radiation-induced defects undergo strain-induced migration. With increasing nitridation, an increasing amount of nitrogen is incorporated in the interface. The interfacial region is less strained because of the presence of nitrogen. As a result, the number of strained bonds at the interface and the width of the interface are reduced.

Diodes nitrided at 1065 °C showed higher radiation hardness compared with diodes nitrided at 1165 °C. This is consistent with the viscous shear flow model proposed by EerNisse and Derbenwick [14].

As seen in Figure 2, the radiation-induced change in the quantum efficiency of the most stable nitrided diode is less than 4% at a photon fluence of $10^{16}/cm^2$. (The diode active areas were underfilled during exposures; fluences have been normalized to 1 $cm^2$.) The absorbed dose in the $SiO_2$ may be calculated as follows.

Figure 3 indicates that 78% of the incident photons ($10^{16}$ photons/$cm^2$, in this case) are absorbed in 5 nm thick $SiO_2$. (One finds negligible reflection from the front surface of 5 nm of $SiO_2$ on Si at 10.2 eV [121.6 nm] when calculations are made using the Fresnel equations and published optical constants [8].)

Total photons absorbed per unit volume in 5 nm of oxide = ($7.8 \times 10^{15}$ photons/$cm^2$) / ($5 \times 10^{-7}$ cm) = $1.56 \times 10^{22}$ photons / $cm^3$

Energy absorbed per unit volume = ($1.56 \times 10^{22}$ photons/$cm^3$) x (10.2 eV/photon) x ($1.6 \times 10^{-19}$ J/eV) x ($10^7$ erg/J)

$$= 2.55 \times 10^{11} \text{ erg / cm}^3$$

Energy absorbed per unit mass = ($2.55 \times 10^{11}$ erg / $cm^3$) / (2.2 g/$cm^3$)

$$= 1.16 \times 10^{11} \text{ erg / g}$$

$$= 1.16 \times 10^{9} \text{ rad} = 1.16 \text{ Gigarad}$$

$$(1 \text{ rad} = 100 \text{ erg/g} = 10^{-2} \text{ J/kg})$$

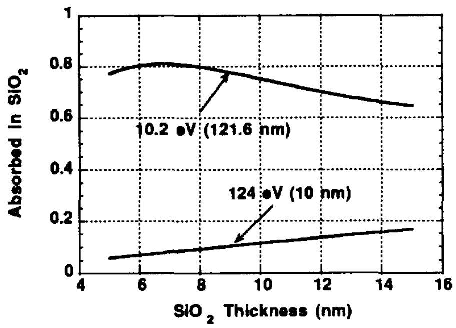


Fig. 3 Absorption of radiation in $SiO_2$ on a silicon substrate as a function of oxide thickness at two photon energies. Calculated using the Fresnel equations using optical constants from Ref. [8].

Thus, fabrication of 1 Gigarad hard silicon dioxide has been demonstrated. To the best of our knowledge, this is the hardest oxide ever reported or known to exist in any commercial device.

By definition, quantum efficiency is directly proportional to the photogenerated current, $I_{ph}$. Hence any change in quantum efficiency can be expressed as a change in $I_{ph}$. Radiation-induced interface states will generate a surface recombination current of minority carriers ($I_S$), which will be deducted from $I_{ph}$. The surface recombination current can be written as $I_S = qSpA$, where q is an elemental electronic charge, p is the hole density in the surface region, S is the surface recombination velocity, and A is the device area, which in our case is 1 $cm^2$. The surface recombination velocity is directly proportional to the area density of the interface trapping centers ($N_{it}$). As the diodes had zero surface recombination before being irradiated [2,3,5,6], it may be argued that the post-irradiation surface recombination current is caused by an increased number of interface traps.

The S and $N_{it}$ are related by $S = \sigma_p V_{th} N_{it}$ [15], where $\sigma_p$ is the hole capture cross section, and $V_{th}$ is the thermal velocity. Therefore, an increase in $N_{it}$ will increase S, and this, in turn, causes degradation in the quantum efficiency.

Quantitatively, the post-exposure quantum efficiency may be modeled as follows:

$$I_{ph} = I_0 - I_S \tag{1}$$

in which $I_0$ is the initial photogenerated current (with near-theoretical quantum efficiency).

Let

$$I_S = qSpA = K''S \tag{2}$$

where K" is a constant, and let

$$S = \sigma_p V_{th} N_{it} = K'N_{it} \tag{3}$$

where K' is another constant.

Let $N_{it} \alpha D^n$ [15,16], where D, the dose, is in Mrad.

Therefore,

$$I_{ph} = I_0 - KD^n \tag{4}$$

or

$$(I_0 - I_{ph}) = KD^n \tag{5}$$

Using the experimental values of $I_0$ - $I_{ph}$ and D from Fig. 2 (a), the above equation has been plotted, and is shown in Fig. 4. The values of n and K from this figure are 0.9 and 6.026 x $10^{-5}$, respectively. It may be pointed out here that n values as large as 0.95 have been reported in the literature [15].

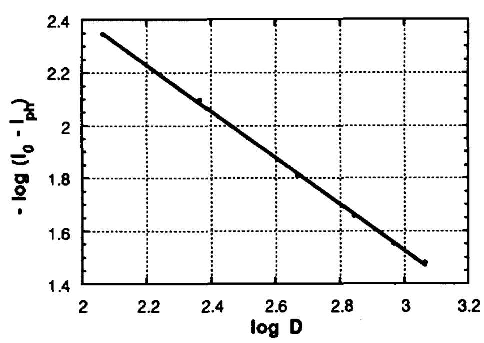


Fig. 4 Dependence of the quantum efficiency degradation (reduction in photogenerated current from theoretical values) on dose, D. The dose is in Mrad.

Figure 5 shows the effect of 124 eV exposure on the diode quantum efficiency. This figure clearly shows that there is no change in the quantum efficiency, and hence no radiation-induced traps have been generated up to a dose of 188 Mrad. Extension of the data with higher dose is being carried out presently, which will lead to information on the dependence of defect generation on photon energy.

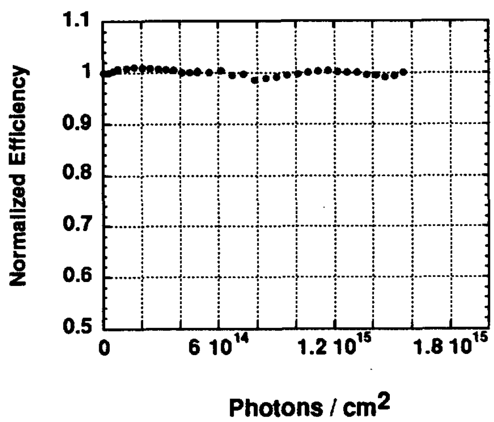


Fig. 5 Effect of 124 eV photon exposure on the quantum efficiency of a nitrided photodiode.

Other investigators have reported that the number of defects generated depends only on the absorbed dose, and not on the energy of the incident radiation [17] when Al Kα (1.49 keV) and Cu Kα (8.03 keV) photons were used.

Impurity diffusion models postulated by other investigators [11] suggest that nitrided oxides may have reduced degradation over as-grown oxides in the presence of water vapor. This would be of importance in many applications, such as radiometry, in which changes in the effective thickness of the oxide would have an impact. Figure 6 shows that the nitrided oxide diode quantum efficiency in the 50–250 nm wavelength region did not change after exposure to 100% relative humidity for 4 weeks. This is in marked contrast with our previous observations [18] where diodes with as-grown $SiO_2$ had exhibited more than 10% degradation in quantum efficiency. Thus, it may be concluded that the nitrided Si-$SiO_2$ is practically insensitive to moisture.

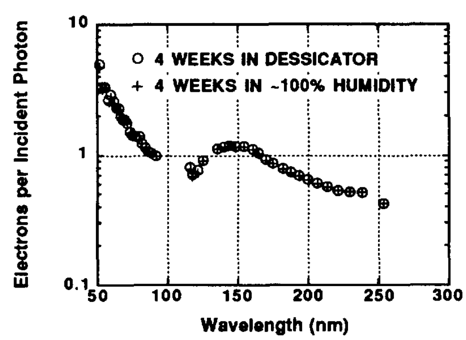


Fig. 6 Effect of water vapor on the efficiency of silicon photodiodes treated with nitrous oxide as a function of wavelength in the XUV.

## IV. CONCLUSIONS

Silicon photodiodes with nitrided passivating silicon dioxide coatings were found to be several times more resistant to ionizing radiation compared with diodes with thermally grown oxide. Radiation resistance of the nitrous oxide nitrided diode was over 1 Gigarad. The higher radiation resistance of the nitrided diodes may be explained using the bond strain gradient model of Grunthaner et. al [13]. The buildup of the radiation-induced interface trap density was found to be sublinear with dose at the rate of $D^{.9}$. The developed oxide hardening technique deserves further investigation to assess its applications to other silicon devices. Nitrogen incorporation in the Si-$SiO_2$ interface was found to make it practically insensitive to moisture.

## V. REFERENCES


[1] R. Korde and L. R. Canfield "Silicon Photodiodes with Stable, Near Theoretical Quantum Efficiency in the Soft X-ray Region," in *Proc. Symposium on X-ray Instrumentation in Medicine and Biology, Plasma Physics, Astrophysics and Synchrotron Radiation, SPIE*, vol. 1140, pp. 126–132 (1989) and references cited therein.

[2] R. Korde and J. Geist, "Stable, High Quantum Efficiency UV-Enhanced Silicon Photodiodes by Arsenic Diffusion," *Solid State Electronics*, vol. 30, pp. 89–92 (1987).

[3] R. Korde and J. Geist, "Quantum Efficiency Stability of Silicon Photodiodes," *Applied Optics*, vol. 26, pp. 5284–5290 (1989).

[4] L. R. Canfield, J. Kerner, and R. Korde, "Stability and Quantum Efficiency Performance of Silicon Photodiode Detectors in the Far Ultraviolet," *Applied Optics*, vol. 28, pp. 3940–3943 (1989).

[5] D. E. Husk et al., "Response of Photodiodes in the Vacuum Ultraviolet," *Journal of Applied Physics*, vol. 70, pp. 3338–3344 (1991).

[6] Jon Geist, A. M. Robinson, and C. R. James, "Numerical Modeling of Silicon Photodiodes for High-Accuracy Applications Part III, Interpolating and Extrapolating Internal Quantum Efficiency Calibrations", *J. Res. Nat'l Jnst. of Stds. and Tech.*, vol. 96, pp. 481–492 (1991).

[7] S. Yoon and M. White, "Study of Thin Gate Oxides Grown in an Ultra-Dry Clean Triple-Wall Oxidation Furnace System," *J. Electronic Materials*, vol. 19, pp. 487–493 (1990).

[8] Edward D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, 1985.

[9] R. J. Powell and G . F. Derbenwick, "Vacuum Ultraviolet Radiation Effects in $SiO_2$," *IEEE Transactions on Nuclear Sciences*, vol. NS-18, pp. 99–105 (1971).

[10] L. R. Canfield and N. Swanson, *Journal of Research of the National Bureau of Standards*, vol. 92, pp. 97–112 (1987).

[11] For example, see: H. R. Harrison and S. Dimitrijev, "Ultrathin Dielectrics for Semiconductor Applications — Growth and Characteristics," *Microelectronics Journal*, vol. 22, pp. 3–38 (1991), and references cited therein.

[12] Y. Okada et al., "Evaluation of Interfacial Nitrogen Concentration of RTP Oxynitrides by Reoxidation," *Journal of the Electrochemical Society*,, vol. 140, pp. L87–L89 (1993).

[13] F. J. Grunthaner, P. J. Grunthaner and J. Maserjian, "Radiation Induced Defects in $SiO_2$ as Determined with XPS," *IEEE Transactions on Nuclear Sciences*, vol. NS-29, pp. 1462–1466 (1982).

[14] E. P. EerNisse and G. P. Derbenwick, "Viscous Shear Flow Model for MOS Device Radiation Sensitivity," *IEEE Transactions on Nuclear Sciences*, vol. NS-23, pp. 1534–1539 (1976).

[15] T. P. Ma and Paul V. Dressendorfer, *Ionizing Radiation Effects in MOS Devices and Circuits*, John Wiley and Sons, 1989.

[16] J. M. Benedetto, H. E. Boesch, Jr., and F. B. McLean, "Dose and Energy Dependence of Interface Trap Formation in Cobalt-60 and X-ray Environments," *IEEE Transactions on Nuclear Sciences*, vol. NS-23, vol. 35, pp. 1260–1264 (1988).

[17] A. Reisman et. al "Low Energy X-ray and Electron Damage to IGFET Gate Insulators," *Journal of the Electrochemical Society*, vol. 131, pp. 1404–1409 (1984).

[18] L. R. Canfield, NIST, unpublished work.


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