

CCD Detection of 157 nm Photons

Flora Li ^{*a}, Nixon O ^b and Arokia Nathan ^a

^a Department of Electrical and Computer Engineering, University of Waterloo,
Waterloo, ON, Canada N2L 3G1

^b DALSA Inc., 605 McMurray Road, Waterloo, ON, Canada N2V 2E9

* Correspondence: Email: fli@venus.uwaterloo.ca; Tel.: (519) 883-0479; Fax: (519) 746-6321

Abstract

To accommodate the growing demands for imaging at deep-UV (DUV) wavelengths, particularly in semiconductor inspection systems, there is a quest for new deep-UV sensitive CCD sensors. This paper reports on the response measurements of frontside-illuminated linear CCD's to 157-nm photons. The dielectric layers on top of the imaging region have been etched to improve deep-UV sensitivity. Although the CCD's are stable when exposed to visible wavelengths, the dark current varies almost exponentially with exposure dose at 157-nm and an enhancement in quantum efficiency (QE) is observed with extended exposures. The change in dark current depends on UV fluence and interface properties. It is believed that UV photons are absorbed in the oxide to cause structural modifications in the oxide layer and at the interface, which results in shifts in device performance.

1. Introduction

In order to facilitate the inspection of deep sub-micron features on wafers and photomasks, the new generation of semiconductor inspection systems is being pushed to image at increasingly lower UV wavelengths. CCD cameras that are sensitive to deep-UV are an asset to these wafer inspection systems. However, the development of such devices with high UV sensitivity and good long-term stability is not straightforward. Conventional CCD cameras have very poor responsivity in the deep-UV because of the short absorption depth of UV photons in silicon coupled with the strong UV absorption in the frontside of the structures. Where cameras are responsive in the deep-UV, their long-term stability is a major concern.

Frontside-illuminated UV cameras that are stable at 248 nm are now available. In this paper, we investigate the behaviour of frontside-illuminated CCD structures when exposed to 157-nm photons from F₂ excimer laser irradiation. The IC industry anticipates that by 2005, F₂ excimer laser ($\lambda = 157\text{-nm}$) may be used for a new generation of optical lithography systems that can realize the 70-nm-node feature sizes. Thus, CCD cameras that are sensitive deeper into the UV must be developed to keep up with the new advancements in lithography.

2. Thinned Frontside CCD Structures

Studies on radiation damage suggest that many UV degradation artifacts in devices with Si-SiO₂ layers are linked to UV-induced effects in the oxide layer [1]. In CCD cameras, thinning the overlying oxide layer may alleviate some of the UV degradation issues. A reduced oxide volume will lessen the interaction of UV photons with the oxide. This is expected to improve the QE and stability of CCD sensors at deep-UV wavelengths.

We fabricated and tested two types of deep-UV frontside-illuminated linescan CCD's with thin oxide over the pixels. The two have different oxide thickness and interface quality, as we will discuss shortly. The sensors employ a two-phase buried-channel CCD shift registers and have 512 14- μm square pixels. The photosensitive region is a pn-junction photodiode with the oxide overlayers partially removed to improve UV sensitivity. These samples have oxide thicknesses of approximately 1398 Å and 724 Å. The device with thinner oxide is fabricated using a different process recipe that exposes the silicon surface to aluminum, and possibly other impurities, during processing. The device with the thicker oxide is not similarly

exposed. Thus, the former exhibits poorer Si-SiO₂ interface quality. A cross-section of the two types of pixels is illustrated in Figure 1.

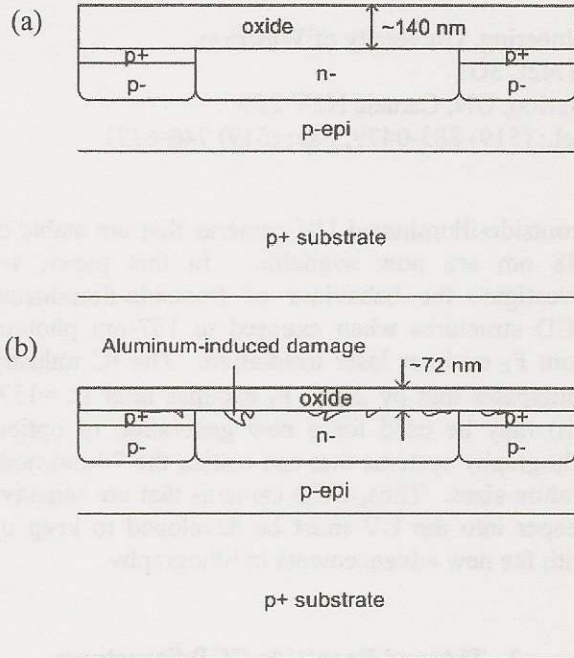


Figure 1. Cross-section of the etched photosite. (a) Sample 1 has thicker oxide and better interface quality. (b) Sample 2 has thinner oxide but poorer interface quality. Dimensions are not drawn to scale.

The devices are exposed to 157-nm F₂ excimer laser at intensities ranging from 0.2 to 10 pJ/pulse. The pulse frequency is 100 Hz and the pulse width is 15-ns. Quantum efficiency (QE) measurements are first performed at 0.2 pJ/pulse to ensure the sensors are not in saturation. The response is monitored for approximately an hour. Next, the sensors are exposed to a laser intensity of 10 pJ/pulse for accelerated degradation testing. The experimental setup is illustrated in Figure 2.

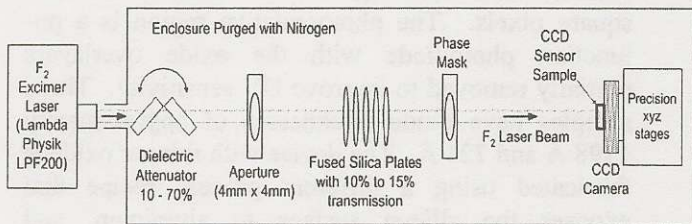


Figure 2: Experimental setup for 157-nm measurement.

3. QE Fluctuations

Experiments demonstrate that CCD samples with thinner overlying oxide exhibit higher QE at 157-nm because of the decreased UV absorption in the oxide layer. In general, we observed the QE to be a function of laser frequency and intensity. More importantly, we observed QE fluctuations that are dependent on the UV dose. This is illustrated in Figure 3. The QE at 157-nm increases with continuous exposure, but decreases after a momentary interruption. The data also reveal that the rate of change in QE is a function of the laser intensity.

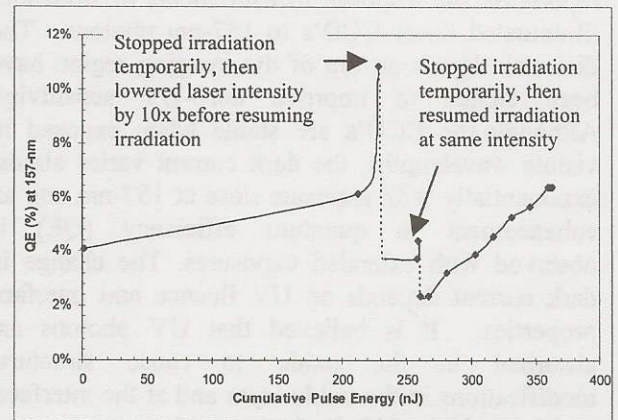


Figure 3. Temporal fluctuations of the QE at 157-nm.

The QE fluctuations observed may be caused by a number of factors [2], including UV-induced bond structure rearrangement in the oxide, UV-induced absorption in the oxide due to color center formation, generation of charged centers in the oxide, and interface modification. Some of these are time- or dose-dependent, as reported in the literature. For example, Ikuta *et al.* [3] reported that the UV-induced absorption intensity in SiO₂ is a function of the accumulative fluence of deep-UV irradiation, and suggested that the observed changes are caused by the formation and restoration of color centers. This variation in the induced absorption of SiO₂, along with other photo-induced effects, will influence the deep-UV stability of the CCD sensor. In general, these UV-induced effects alter the optical and electrical properties of the oxide and interface layers, resulting in both temporary and permanent

shifts in device performance. In the following section, we will discuss possible reasons for the observed enhancement and reduction in QE. We will defer the discussion of UV-induced color center formation in the oxide until Section 5.

QE Enhancement

QE enhancement may be attributed to four possible mechanisms.

- ◆ Because the F₂ laser has a photon energy of 7.9-eV, which is close to the optical band-gap energy of amorphous SiO₂ (8 to 9 eV depending on the temperature and process chemistry used to form the oxide [1]), a portion of the incident 157-nm photons can get absorbed in the SiO₂ layer. After absorption, photo-generation of electron-hole pairs may occur in the oxide. Some of the electrons excited from the valence band to the conduction band of the oxide may drift to the silicon layer, where they add to the number of signal electrons collected. This will increase the measured extrinsic QE.
- ◆ Multi-photon absorption processes can also contribute to QE fluctuations. Continuous exposure to deep-UV laser enables electrons in the oxide to be excited to higher energy levels via successive photon absorption. With this process, more electrons can gain sufficient energy to enter the conduction band and contribute to conduction processes, leading to enhanced QE. At higher laser intensity, more photons per laser pulse are absorbed by the CCD, and multi-photon absorption is more likely to occur. This is in agreement with our observation that QE enhancement is greater at higher laser intensity.
- ◆ There is the possibility that the absorbed 7.9-eV photons may have sufficient energy to induce structural modifications in the oxide and/or in the Si-SiO₂ interface. Instances of laser-induced structural changes by KrF ($\lambda = 248$ nm) excimer laser irradiation in SiO₂ material and at the Si-SiO₂ interface have been reported by Fiori and Devine [4] and by Lu *et al.* [5] respectively. The UV laser photons may rearrange the bonds between silicon and oxygen or between these elements and oxide impurities, causing reduced optical absorption in the SiO₂ layer. Reduced

oxide absorption will result in an increase in photon absorption in silicon, thus an enhancement in QE. The deep-UV laser may also modify interface properties by triggering bond structure rearrangements (e.g., changes in bond angles and bond lengths) at the interface. These interfacial modifications may result in a bond arrangement that disfavors electron trapping events by interface states, thus improving the QE at 157-nm.

- ◆ The UV photons absorbed in SiO₂ may produce charge species in the oxide layer that modify the electrical properties of the oxide. Photo-induced fixed oxide charge modification in SiO₂ has been reported by Fiori *et al.* [6]. They observed that the fixed oxide charge density is a function of the accumulative UV dose. It is possible that negatively charged centers are induced in SiO₂, causing positive charge carriers (holes) to accumulate at the Si-SiO₂ interface. This layer of holes occupies the interface states, reducing the trapping or recombination of photo-generated electrons at the interface, which increases the number of signal electrons collected, and hence leading to higher QE.

Because of the intricate nature of the mechanisms involved, it is difficult to determine which process is dominant. It is likely that all processes described above occur concurrently. More in-depth research and investigation are required to generate a unified model of UV-induced QE enhancement.

QE Reduction after Interruption

As shown in Figure 3, QE decreases after a momentary interruption. The causes for the temporal QE reduction may be associated with relaxation/restoration processes of defect centers in the oxide and/or at the interface. The possible mechanisms are discussed below.

- ◆ As discussed earlier, UV irradiation can cause negatively charged defect centers to form in the oxide. This in turn induces a layer of holes at the interface, shielding the signal electrons from the interface traps. If these negatively charged defect centers relax or become neutral due to recombination when irradiation terminates, the holes in the Si layer may drift away from the interface and the signal electrons are no longer

shielded from the interface states. Thus, electron trapping may occur when irradiation resumes. An increase in electron trapping leads to a decrease in QE when irradiation resumes after a temporary interruption.

- ◆ During continuous exposure, electrons are excited to progressively higher energy states via multiple photon absorption processes. When irradiation is interrupted, the electrons that have been excited to mid-band energy levels in the oxide will eventually decay back to the ground state. Since the majority of electrons will be at ground state when irradiation resumes, a much smaller population of electrons is available to be excited from the mid-band energy levels into the conduction band at this point. Hence, the QE after interruption will initially be lower than the QE before interruption.
- ◆ The decrease in QE can also be related to the dynamics of interface trapping. The interface traps may be fully occupied during continuous UV irradiation. Since the interface no longer traps electrons, any additional electrons generated will only contribute to the response signal. When irradiation terminates, the trapped charges may be freed from the interface states. Some of the unoccupied interface states will trap signal electrons, leading to a drop in the QE when UV irradiation is resumed.

Again, it is not clear which mechanism is dominant. More extensive investigation is required to identify the underlying causes of QE fluctuations in CCD's after 157-nm F_2 laser irradiation.

4. Dark Current Measurements

To investigate the effect of higher laser intensity, the CCD's are exposed to laser irradiation of 10-pJ/pulse. The key observation here is that the dark current increases almost exponentially as a function of 157-nm exposure dose, as shown in Figure 4. CCD's with inferior interface quality exhibit greater dark current instability. We observed that the dark current of the CCD sample with inferior interface quality increases by about 30 times after only 15 minutes of irradiation at 10 pJ/pulse.

We also observed that the rate of dark current increase is a function of the laser intensity. Here, the two pixels that receive the same cumulative dose but at different laser intensities per pulse experience different levels of increase in dark current.

Because the 157-nm photons are absorbed very close to the interface in the silicon layer and because we observed a dependence of dark current on interface quality, it is highly likely that the increase in dark current is a result of the UV-induced changes in the Si-SiO₂ interface.

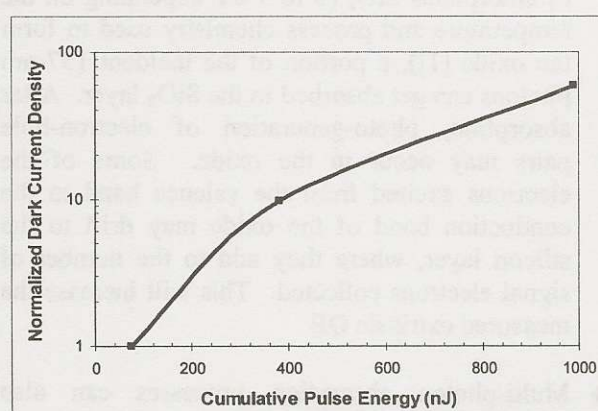


Figure 4. Dark current density as a function of exposure to 157-nm radiation. The pixel shown has been exposed to 10 pJ/pulse. Values are normalized to the level prior to exposure.

Interestingly, UV exposure can also reduce the dark current at low laser intensities. When a previously unexposed CCD sample with inferior interface quality is irradiated with 157-nm laser at 1.4-pJ/pulse, the dark current density decreased substantially after only 2 minutes of exposure. This may be attributed to a decrease in the interface state density due to UV-induced interface modification or UV-induced charging effects in the oxide. The 157-nm photons absorbed in SiO₂ can induce negatively charged centers in the oxide layer, causing positive carriers to accumulate at the Si-SiO₂ interface. This layer of holes can result in a reduction in the dark current.

The dark current can continue to change weeks after the last 157-nm exposure. This is illustrated in Figure 5. We believe that the relaxation and/or rearrangement of UV-induced defects in the oxide and interface layers can occur over longer time

periods, resulting in a gradual reduction in the dark current.

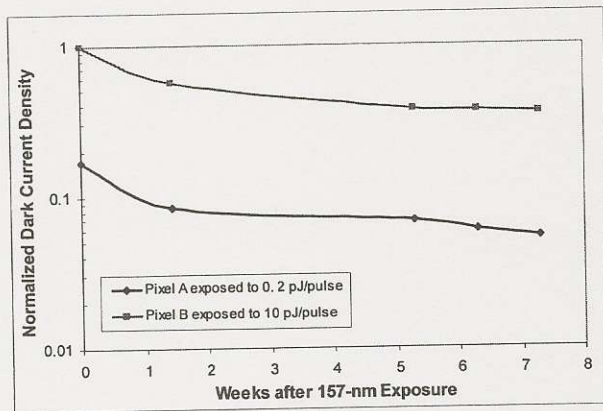


Figure 5. Long term change in dark current following 157-nm exposure. Dark current density is normalized to the value of pixel B just after exposure.

The above observations suggest that the radiation-induced changes in dark current depend strongly on the UV fluence and on the interface properties. It appears that different laser intensities have different effects on the CCD stability and dark current characteristics.

5. UV-Induced Oxide Effects and Color Center Formation

The primary radiation damage effects in SiO₂ are induced absorption associated with color center formation and structural changes related to densification or compaction [7]. Both of these events can lead to changes in the optical and electrical properties of the CCD sensor, which in turn influence the overall device performance.

Some of the incident 157-nm photons that are absorbed in the oxide interact with bonds and impurities to create defect centers. The main defect species created by F₂ excimer laser irradiation in SiO₂ are the color centers identified as E' center and non-bridging oxygen hole center (NBOHC) from the photolysis of strained Si-O-Si bonds:



The E' center ($\bullet \text{Si} \equiv$) is an under-coordinated silicon atom with an absorption band centered at 5.7-

eV. The NBOHC ($\equiv \text{Si} - \text{O}^{\bullet}$) is a hole trapped on an oxygen atom with absorption bands centered at 4.8 eV and 6.4 eV. The concentration of these color centers, or equivalently the induced absorption coefficient of SiO₂, changes as a function of cumulative deep-UV exposure. The relaxation and restoration processes of color centers have also been reported to cause fluctuations in the optical absorption of SiO₂ material [3]. Since optical properties of the SiO₂ layer in CCD's may change with exposure dose, it is likely that the CCD performance will also be affected. Indeed, this instability is observed in the measurements where the QE fluctuates with accumulative 157-nm exposure.

6. Conclusion

We present a thinned frontside-illuminated linear CCD structure designed for deep-UV imaging applications. We have shown that the thinned CCD structures are responsive at 157-nm, but the stability needs to be improved. The 157-nm experimental results suggest that the oxide overlayer thickness and the Si-SiO₂ interface quality are important factors that determine many of the CCD performance parameters (such as responsivity and long-term stability) in the deep-UV. Because incident UV radiation is absorbed close to the Si-SiO₂ interface, careful control of the interface quality, with an effort to minimize interface states density, is critical for improving the deep-UV performance of CCD sensors. The experimental results also demonstrate that the thinned frontside-illuminated CCD's may yet provide a low-cost alternative for deep-UV imaging. Nevertheless, further optimization of the oxide thickness and interface quality are necessary to obtain sensors with the desired performance at deep-UV wavelengths.

7. References

- [1] W. W. Duley, *UV lasers: effects and applications in materials science*, Cambridge University Press, New York, 1996.
- [2] E. M. Dianov *et al.*, "UV Irradiation-Induced Structural Transformation in Phosphosilicate

Glass," *J. Non-Crystalline Solids*, Vol. 249, pp. 29-40, 1999,

- [3] Y. Ikuta *et al.*, "Damage behaviour of SiO₂ glasses induced by 193 nm irradiation under a simulated operating mode of lithography laser," *SPIE*, Vol. 4347, pp. 187-194, 2001.
- [4] C. Fiori and R. Devine, "Photo-induced oxygen loss in thin SiO₂ films", *Physical Review Letters*, Vol. 52, No. 23, pp.2081-2083, 4 June 1984.
- [5] Y. L. Lu *et al.*, "Controllable laser-induced periodic structures at silicon-dioxide/silicon interface by excimer laser irradiation", *Journal of Applied Physics*, Vol. 80 No. 12, pp.7052-7056, 5 December 1996.
- [6] C. Fiori, R. Devine and P. Meiland, "Photoinduced fixed oxide charge modification in SiO₂ films", *Journal of Applied Physics*, Vol. 58, No. 2, pp.1058-1060, 15 July 1985.
- [7] J. Moll, "Assessing Damage for UV-Laser-Resistant Fused Silica," *Photonics Spectra*, pp.78-81, April 2002.

...in a gradual reduction in the ...

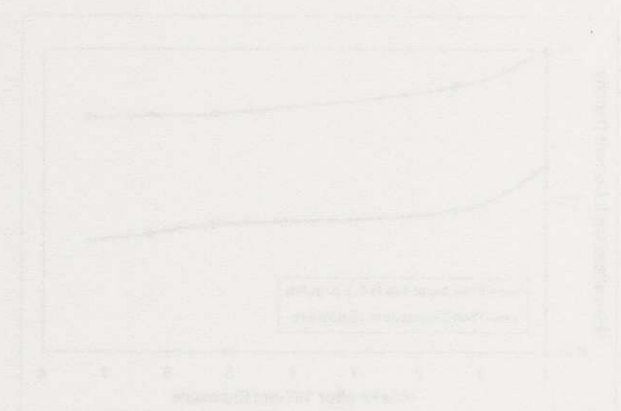


Figure 2. Oxygen loss in SiO₂ films as a function of time and power density. The curves correspond to the two different power densities indicated in the legend.

The above characteristics suggest that the ...
induced charge in the silicon dioxide ...
the UV laser and on the interface ...
appear that different laser parameters have different ...
effects on the CCD sensitivity and that ...
characteristics.

2. UV-Induced Oxide Charge and Color Center Formation

The primary electron damage effect in SiO₂ ...
induced absorption associated with color center ...
formation and structural changes related to ...
irradiation is proportional to the dose of dose ...
events and not to changes in the spatial ...
chemical properties of the CCD sensor, which is ...
not between the overall device performance.

Some of the earliest UV-ray photoresist that are ...
checked in the color channel with bands ...
important to some device sensors. The two ...
species formed by UV radiation have ...
SiF₄ and the color centers identified as F₂ ...
non-binding oxygen hole center (NOHC) from the ...
photoresist of amorphous SiO₂ [1].



The F₂ center (F₂⁺) is an interstitial ...
associated with an absorption band centered at 2.7 ...