Delta-doped CCDS as stable, high sensitivity, high resolution UV imaging arrays

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Abstract

Delta-doped CCDS have achieved stable quantum efficiency, at the theoretical limit imposed by reflection from the Si surface in the near UV and visible. In this approach, an epitaxial silicon layer is grown on a fully-processed commercial CCD using molecular beam epitaxy. During the silicon growth on the CCD, 30% of a monolayer of boron atoms are deposited nominally within a single atomic layer, resulting in the effective elimination of the backside potential well. These devices are highly uniform and have exhibited long-term stability. To achieve significantly higher total quantum efficiency, antireflection layers can be directly deposited on the device. This was demonstrated in the 250-400 nm region.

1. Ultraviolet detection with CCDs

Detection of ultraviolet light has numerous strategic and ground and space-based scientific applications. Useful information can be obtained, for example, from the detection of gamma-band radiation of nitrogen oxide (190-280 nm) formed in the high temperature shock layer of h ypervelocity vehicles.[1] The large format and low noise of charge-coupled devices (CCDs) are ideal for these applications. However, the detection of ultraviolet light in Si CCDS has been a long-standing problem, due to the short absorption length of UV photons in silicon. The absorption depth problem is illustrated by Fig. 1, which gives the photon absorption length in crystalline silicon versus wavelength. Note that the absorption depth drops to a minimum of 40 Å at about 270 nm, and is less than 100 Å over the range of wavelengths from 60 nm to 400 nm.

The highest possible quantum efficiency (QE) is obtained by backside-illumination of thinned CCDs. However, positive charge trapped at the Si/SiO_2 interface of a bare silicon surface forms a backside potential well that traps photoelectrons generated near the back surface. For untreated thin CCDS this results in poor and unstable UV quantum efficiency. This backside potential typically extends -0.5 µm into the silicon lattice preventing detection of photoelectrons produced within that region. Treating the back surface of the CCD by negative surface charging (i.e., UV-flooding, bias flash-gating) or ion implantation, has yielded reasonable or high UV quantum efficiency.[2,3] However, these treatments suffer variously from problems of yield, response stability, hysteresis, and long-term reliability. Stability of the quantum efficiency has great impact on ground and space-based applications. Stable quantum efficiency of the device is particularly important in space-based applications where renewal of the back surface treatment (e.g., by exposing the device to intense UV light) is not an attractive option.

In this paper, we describe the growth of delta-doped silicon on commercial CCDS using molecular beam epitaxy (MBE), and the resulting enhancement of the UV quantum efficiency. Deposition of antireflection coatings on delta-doped CCDS is discussed. The characteristics of the modified CCDs, such as the uniformity and stability of the quantum efficiency, are described.

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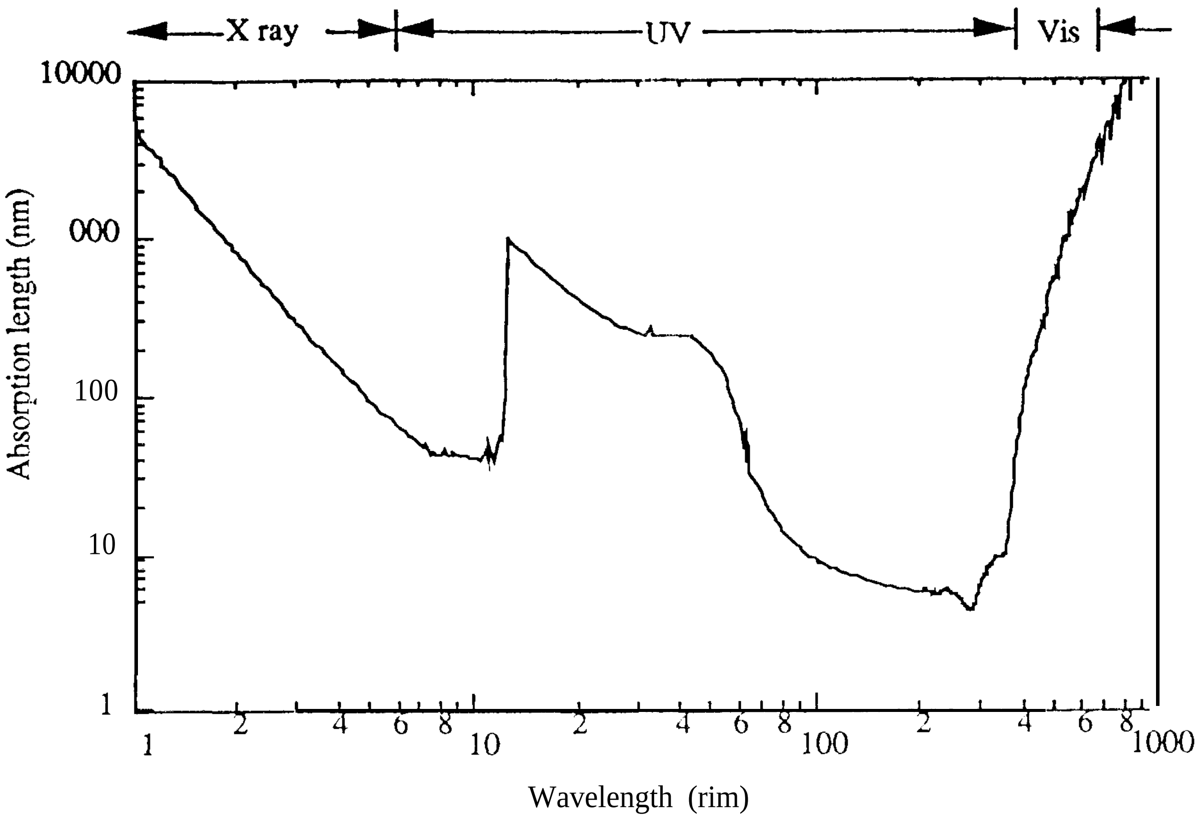

Figure 1. Absorption length in silicon for photons in the x ray, UV and visible regions of the spectrum. The absorption length reaches a minimum of 40 Å in near UV (at a wavelength of 270 rim). At the Lyman α line (121.6 rim), the absorption length is 70 Å.

2. MBE modification of commercial CCDs : Delta-doped CCD process

Using molecular beam epitaxy (MBE), delta-doped CCDs with 100% internal quantum efficiency in the visible and near UV were developed at Jet Propulsion Laboratory.[4] The quantum efficiency achieved by this method is highly stable and exceeds the performance of other reported treatments of backside-thinned CCDs. The quantum efficiency of these devices is limited by the reflection of the photons from the back surface of the device and can be enhanced by deposition of antireflection (AR) coatings on the back surface of the device.

Epitaxial silicon is grown on the carefully prepared back surface of thinned, fully-processed devices. The MBE-grown epilayer, with a thickness of only a few atomic layers, contains an extremely high concentration of p-type dopant (boron) atoms. The boron atoms are incorporated into the lattice approximately 5 Å below the Si-SiO_2 interl'ace, providing the necessary negative charge for band bending at this interface so that the photoelectrons produced are not trapped near the interface and are instead captured in the front potential well. The high concentrations of charge necessary for the removal of the backside potential (at least 10^{14} B/cm^2) and the exacting requirements for its positioning (≤ 10 Å from the interface) can be achieved by MBE but are beyond the scope of ion implantation capabilities. Because of development of low temperature MBE and low temperature substrate cleaning,[5,6] the delta-doping process is possible. During the pre-MBE cleaning and epitaxial growth, the CCD temperature is never raised above 450°C. Exceeding this temperature could cause the diffusion of metal contacts into the silicon and damage the CCD. For example, temperatures exceeding 500°C will damage Reticon

CCDS due to spiking of the Al contacts into the underlying silicon. Also, at this temperature, boron does not diffuse and forms an extremely thin layer of negative charge 5 Å below the Si/SiO_2 interface.

The details of the delta-doping process are described in previous papers.[4,7,8] The major steps of the process are outlined below. Fully-processed Reticon CCD die, complete with aluminum contacts are thinned at Reticon, using gold as a thinning mask.[9] This process leaves the CCD with a thick frame, from which the gold mask has to be removed before MBE. After the gold is chemically removed, the device is cleaned by a series of acids, bases, and solvents to remove contaminants introduced in the gold-removal process.[4] UV-generated ozone is used to remove any remaining hydrocarbon contamination. The thin oxide (~ 15 Å) on the CCD back surface is then removed under N_2 atmosphere by spinning the device at 4000 rpm and dispensing an HF/ethanol solution on the surface. This process results in an atomically clean silicon surface in which the surface atoms are bound to hydrogen atoms. The CCD is then immediately loaded into the MBE chamber and is annealed at low temperature (200°C) for ~5 minutes to remove any physisorbed contaminants. The sample is finally heated to 450°C a few minutes before the growth. The layer structure consists of 10 Å of doped Si, followed by deposition of 2 x 10^{14} B/cm^2, and a final 15 Å layer of undoped silicon. Growth of this layer structure is completed in three minutes. Following the MBE growth, the back surface of the device is oxidized by a 30-minute exposure to steam. Figure 2 schematically shows the delta-doped layer structure grown on the backside of a thinned CCD. Packaging and testing of delta-doped CCDs are performed at Reticon. The results presented in this paper are from MBE-modified Reticon 512 x 512 CCDs.

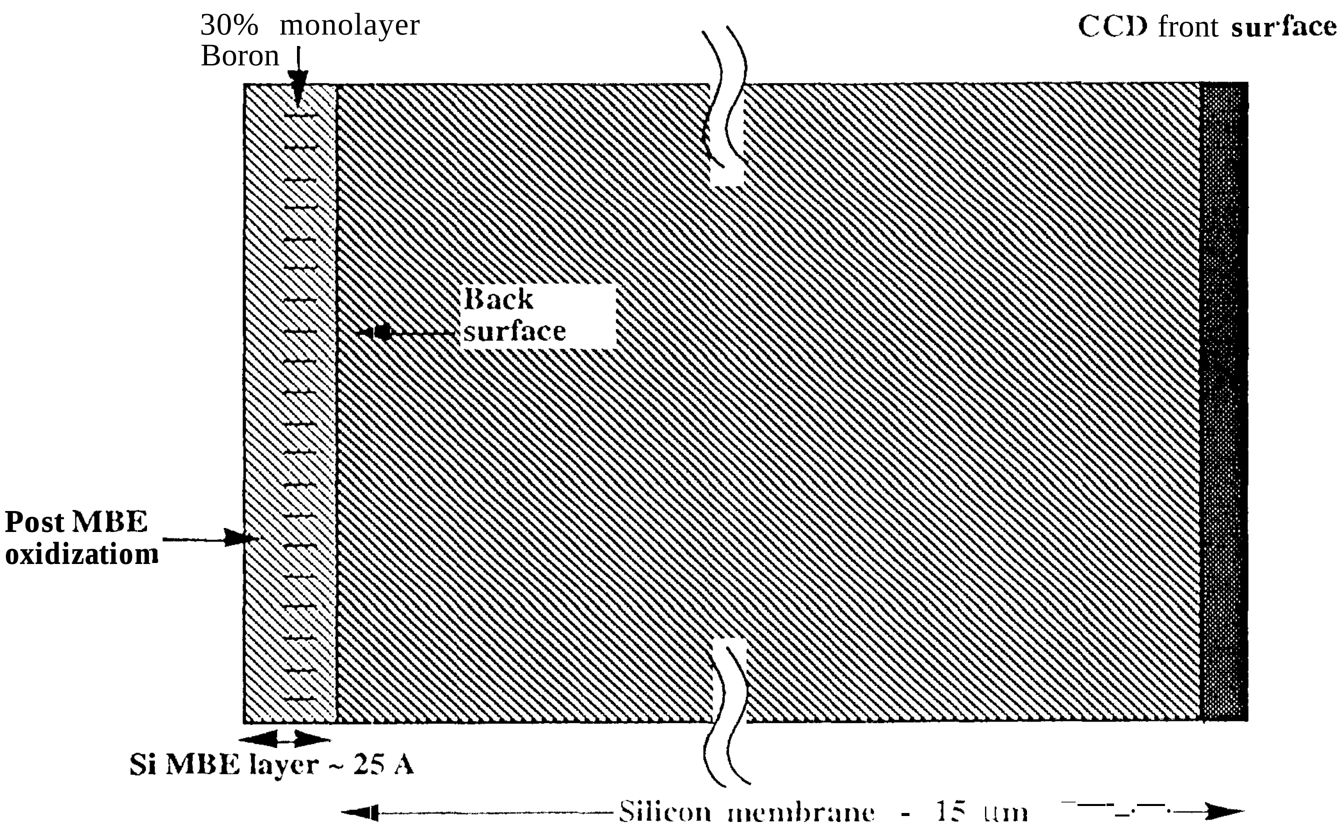

Figure 2 Schematic of the layer structure of a delta-doped CCD, shown in cross section. The layers added by MBE are a total of 2.5 nm in thickness, and contain ~2.5 x 10^{14} p-type dopant (boron) atoms.

3. Quantum Efficiency of Delta-doped CCDs

The CCD quantum efficiency is defined as the number of electrons collected divided by the number of incident photons at a given wavelength. A number of phenomena affect the quantum efficiency. For the purposes of our discussion, these phenomena can be grouped into one of three factors which contribute to the measured quantum efficiency,

$$QE\ (measured) = T \times Internal\ QE \times (QY).$$

T is the transmittance of incident photons into the silicon, which accounts for reflection from the surface and absorption in surface oxides or applied coatings. The quantum yield (QY) is the conversion efficiency of photons to photo-electrons, which is greater than unity for high energy photons ($E \geq 3.5$ eV, $\lambda \leq 350$). A rough estimate of the quantum yield is that one electron-hole pair is produced for each 3.65 eV of photon energy.[10] Internal quantum efficiency is defined as the ratio of the number of the detected photo-electrons to the number of absorbed photons. For a QY of unity, one photo-electron is produced for every absorbed photon, and internal QE could be calculated as the ratio of the measured QE to the transmittance T. In the visible and near UV the transmittance is determined almost entirely by reflection from the bare silicon surface. The internal QE can be affected by trapping or recombination of the photo-elections, e.g., in the backside potential well of the CCD. Figure 3 shows a calculation of the above effects. The solid line is the silicon transmittance, including reflection and absorption in the oxide, and corresponds

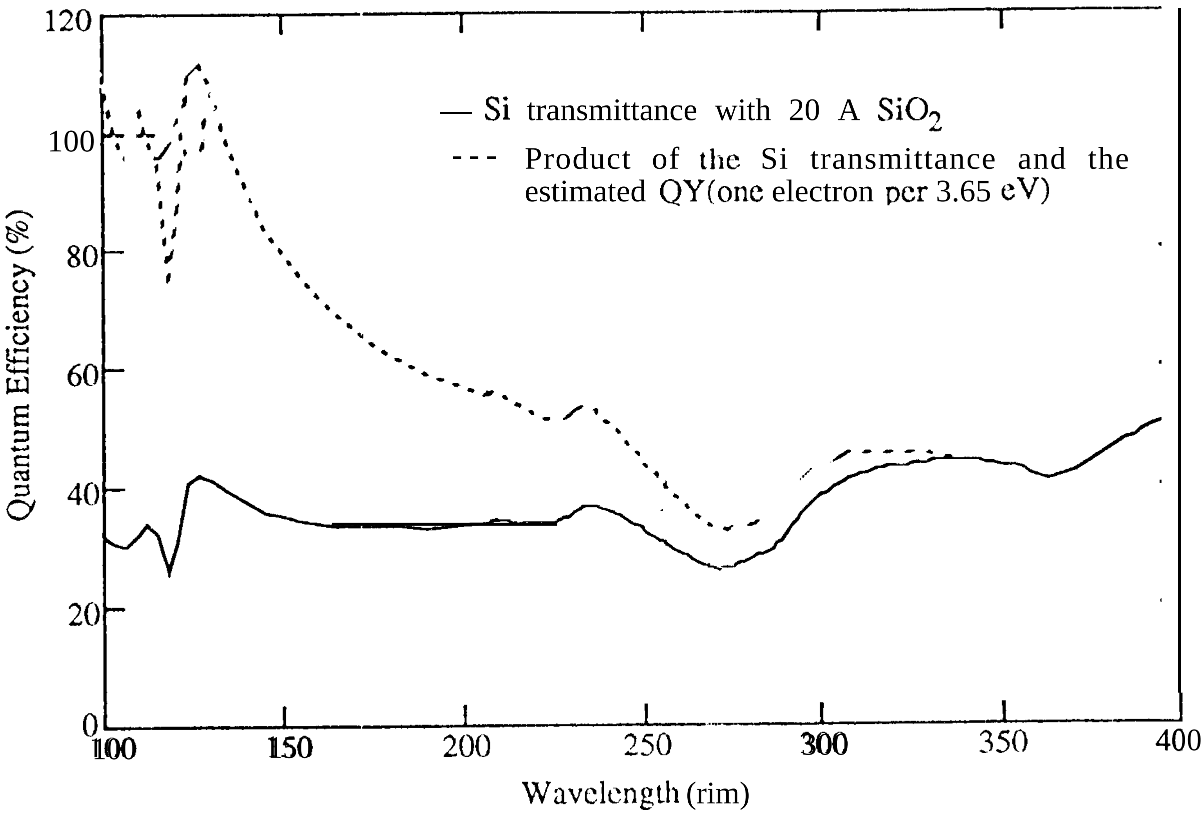

Figure 3. Silicon transmittance including the effect of oxide. Dashed line shows the effect of quantum yield on the quantum efficiency.

to the reflection-limited quantum efficiency (or 100% internal quantum efficiency) for a QY of unity. The dashed line is the silicon transmittance (with oxide) including the effect of quantum yield. For regions of the spectrum where the QY is greater than unity, a measured QE of greater than 1007o is possible.

In addition to the reflection loss from Si surface, there is an additional loss mechanism for the incident photons due to absorption in the thin layer of silicon oxide (15-20 Å). Because the composition and thickness of the oxide are not exactly known, and may in fact change with environmental conditions, it is not possible a priori to calculate the effect of the oxide on the quantum efficiency. Instead, we approximate the effects of the oxide by using glass or quartz optical constants and an average thickness of 20 Å. Absorption in the oxide is negligible for wavelengths greater than 240 nm. For $\lambda \leq 240$ nm, the effect of the oxide becomes significant, and a resonance feature is anticipated to occur in the neighborhood of 120 nm.

The quantum efficiency of delta-doped CCDS has been measured in several different systems. Figure 4 shows the quantum efficiency of two delta-doped CCDs measured at EG&G Reticon. Note that the primary limitation to the internal quantum efficiency is the band structure near the back surface relative to absorption length of photons in silicon, so the most stringent test of the CCD quantum efficiency is the QE at 270 nm, where, as shown in Fig. 1, the minimum absorption length occurs. Data taken at 270 nrn shows that the device performs at 100% internal quantum efficiency at this worst-case wavelength, implying that at lower wavelengths the response will be according to the predictions described in this section. Preliminary QE measurements of delta-doped CCDS at shorter wavelengths (120-250 nm) show that the quantum efficiency of these. devices rises above the reflection-limited QE as the quantum yield rises above unity.

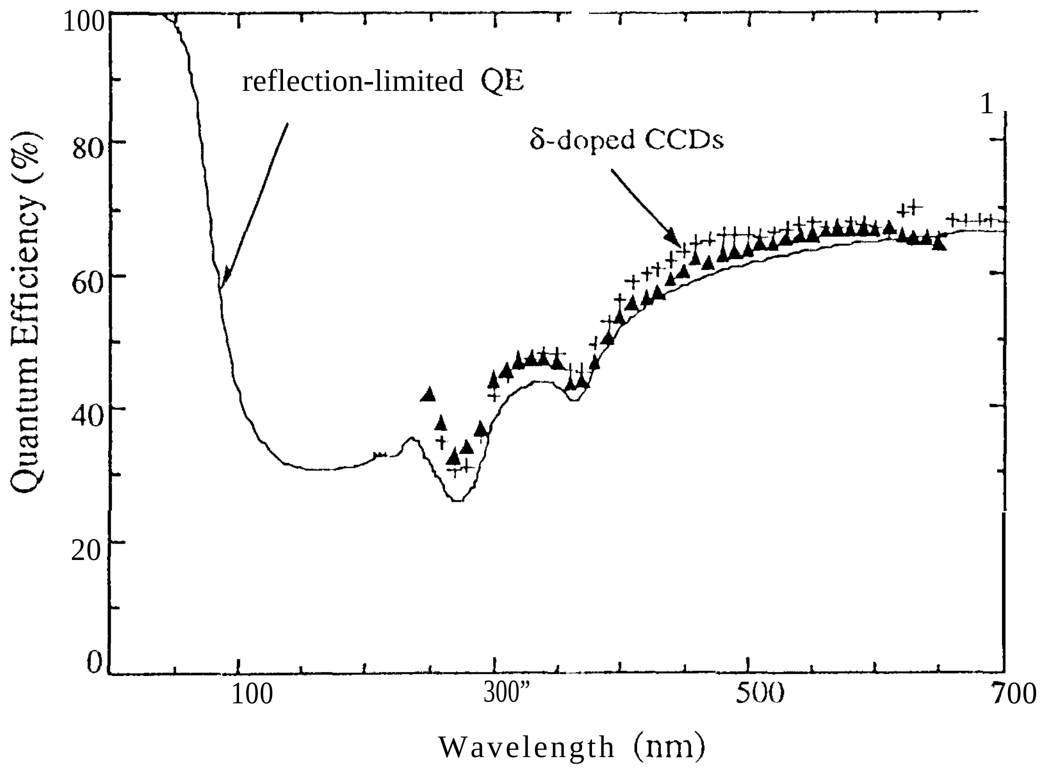

Figure 4. Quantum efficiency of two delta-doped CCDs. Comparison with the reflection-limited quantum efficiency (transmittance of silicon) shows that the delta-doped CCDs exhibit 100% internal quantum efficiency within the uncertainty of the measurement (±5%).

The quantum efficiency of delta-doped CCDS can be further increased by reducing the loss due to reflection. The feasibility of direct deposition of antireflection layers on delta-doped CCDs was demonstrated by depositing two $Hf0_2$ films to enhance the quantum efficiency of two different regions of the spectrum. As mentioned in section 1, the region around 270 nm has important strategic applications and it is also the area of lowest response. For these reasons, a 250 Å thick $Hf0_2$ film optimized to enhance quantum efficiency in this region was chosen for this demonstration. A. 400 Å film was also chosen for enhancement of response in the 300-400 nm region of the spectrum. Using a shadow-masking technique, two separate 3x5 mm^2 areas were used for the deposition of the two films. The rest of the CCD was masked with an Al plate for control purposes. Prior to loading the CCDs in the AR deposition chamber, they were solvent-cleaned to remove hydrocarbons from the back surface of the CCD. Hf02 layers were deposited in University of Arizona's Steward observatory CCD laboratory, using resistive heating to evaporate the $Hf0_2$. This approach avoids the x-ray exposure encountered in e-beam evaporation.[11] Figure 5 shows the response. of the delta-doped CCD in the AR-coated and uncoated areas on the same CCD, together with the theoretical uncoated silicon transmittance curve. Because these are single layer coatings, the AR-coated response will qualitatively follow the characteristic peaks in the Si reflection response. The response of the AR-coated regions show the expected enhancement in the quantum efficiency. The control regions (open circles) were found to respond at the theoretical reflection-limit for bare silicon, indicating that the additional AR coating processes did not degrade the delta-doped structure.

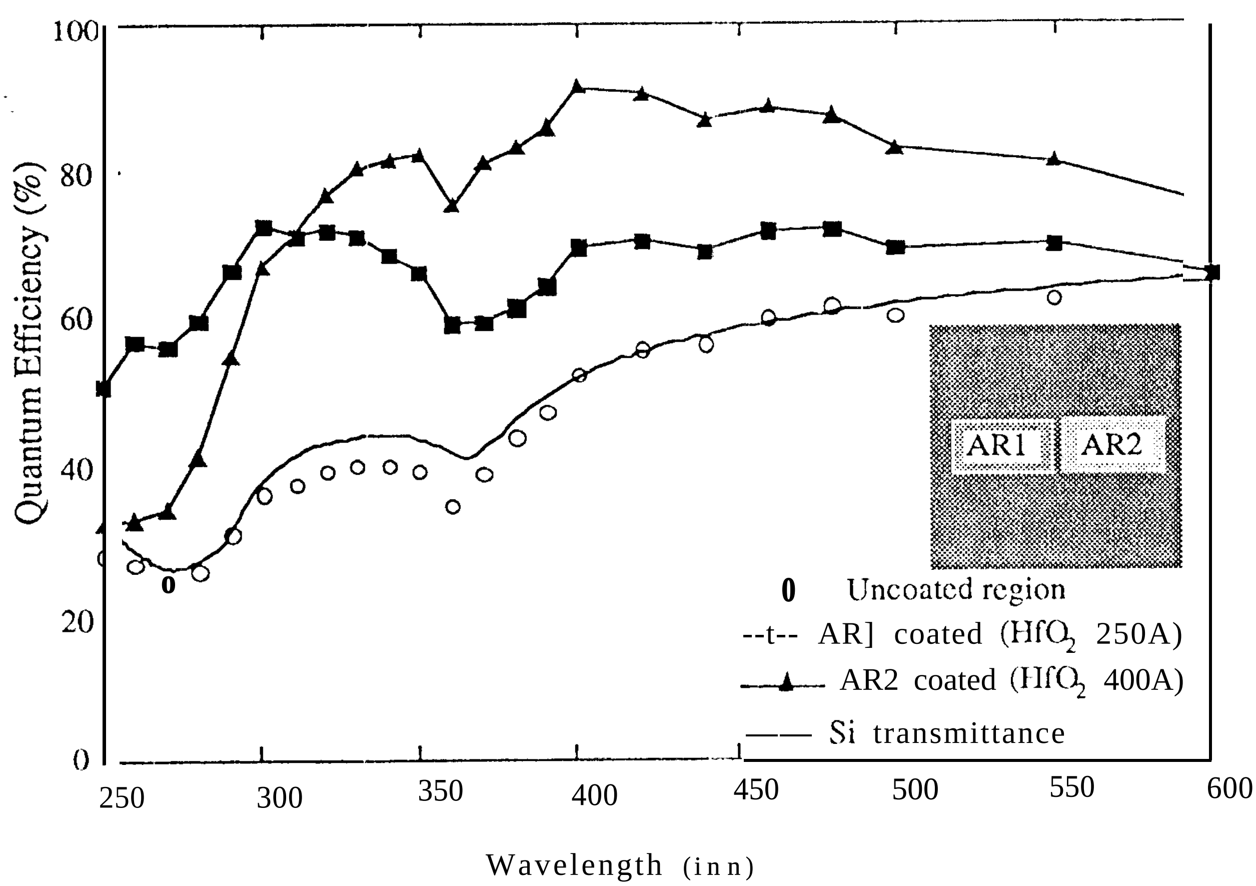

Figure 5 Quantum efficiency data from AR-coated regions of a delta-doped CCD. Two 3x5 mm^2 areas were coated with $Hf0_2$ (250 Å and 400 Å respectively). Data from the uncoated area of the CCD are shown for comparison.

4. Uniformity, stability, and other device characteristics

Delta-doped CCDS exhibit highly uniform, stable response. While it is not possible to directly compare the performance of a single device before and after MBE growth, we will describe characteristics of delta-doped CCDs compared with typical characteristics of standard Reticon CCDS.

The uniformity of the device is demonstrated in Fig. 6 by a typical line plot of the delta-doped CCD taken at 350 nm. The small variations of the response (±3%) shown in the figure, are typical of512 x 512 Reticon CCDS. The flat field response of delta-doped CCDS show high uniformity with only a few blemishes, well within the normal range for the grade of CCDs used in our experiments. The uniformity of the CCD response was also tested by measuring the quantum efficiency in different regions of the same device, as shown in Fig. 7. The measurements on these 50x50 pixel areas were performed at the same time under identical conditions and the quantum efficiencies in the three regions were identical. The inset in the figure shows the approximate position of the three test areas in the array. The pixel-to-pixel variation of the response within each test region is about 1-2%.

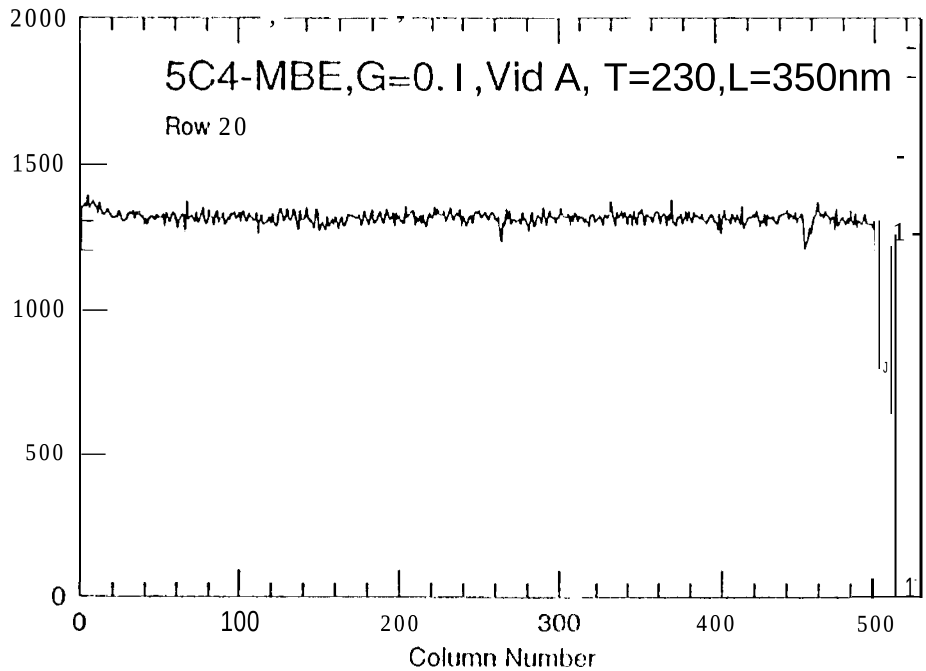

Figure 6. A typical line plot of a delta-doped CCD at 350 nm.

Delta-doped CCDS have been characterized in different measurement setups and have all reported the same 100% internal quantum efficiency. During intervals between QE measurements and deposition of antireflection coatings, the devices have been stored in air in an antistatic box with no further protection. Sixteen months after the MBE process, and after exposure to three different vacuum and camera systems, the quantum efficiency of one of these devices was again measured. Figure 8 exhibits the original and the latest measurements on the device. It should be noted that the two measurements were performed in different systems which each claim, at best, about ±5% precision. Within the accuracy of the measurement, the device has shown no change from the ideal UV response. Although the difference between the two measurements is slightly enhanced in the shorter wavelengths, this is most likely duc to surface contamination from exposure to various systems. Note that unlike UV flooding, no additional backside treatment has been required and the device performance shows no sign of degradation, despite repeated temperature cycling and exposure to different environments.

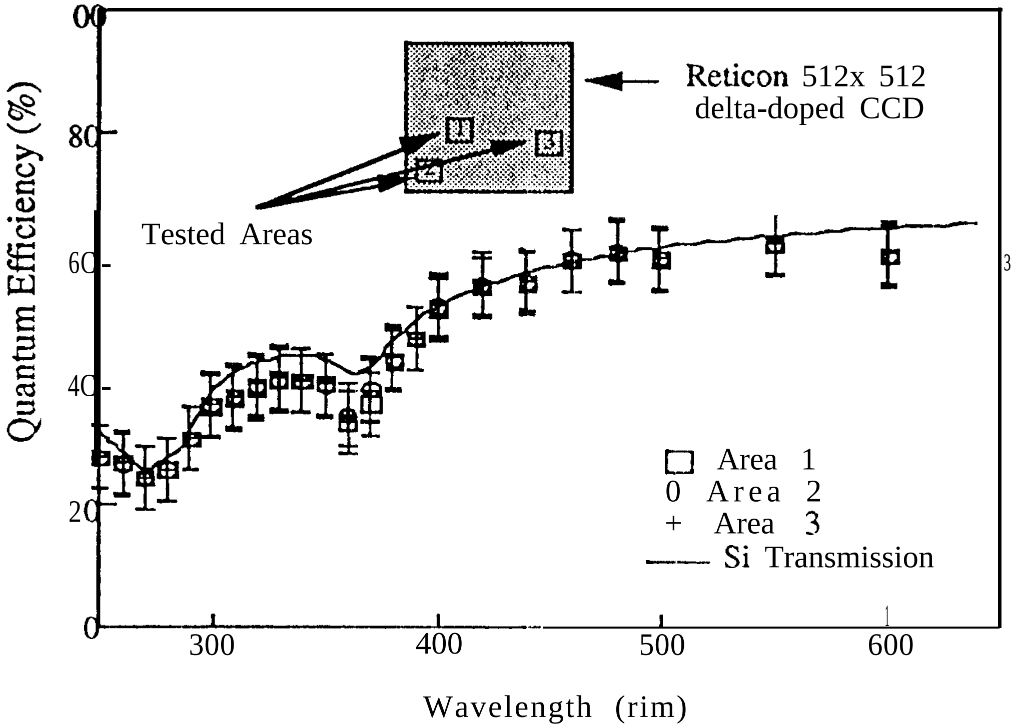

Figure 7. Spectral uniformity of a delta-doped CCD measured on three 50x50 pixel areas of the device. The response m these three regions is identical.

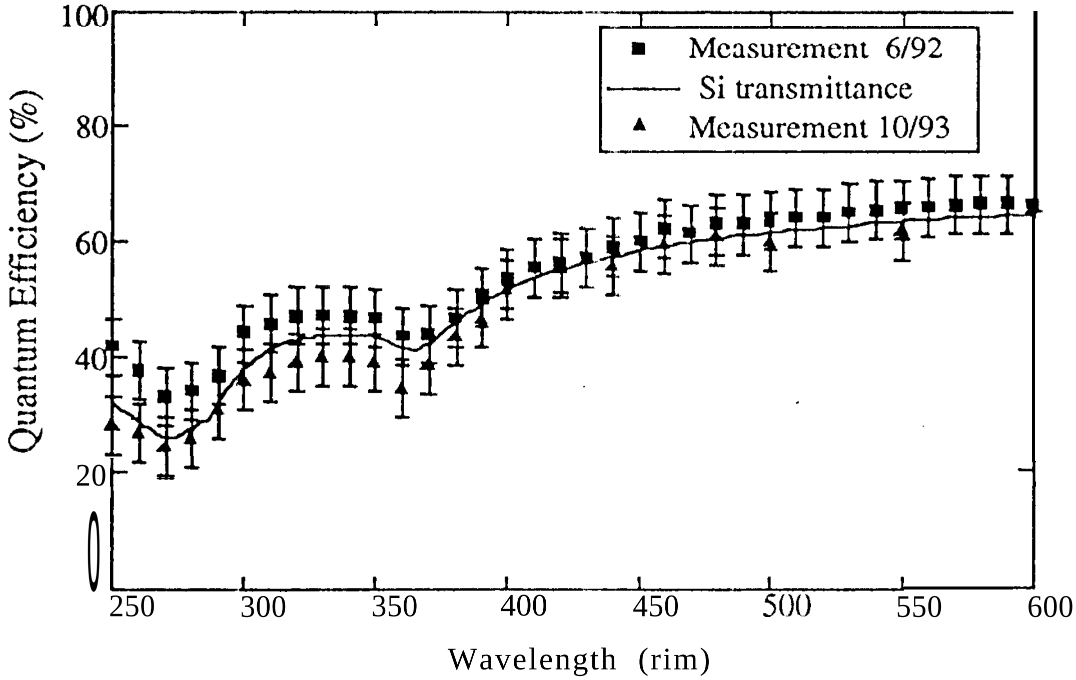

Figure 8 Measurements of a delta-doped CCD made 16 months apart in two different systems show consistent 100% internal quantum efficiency within the limits of uncertainty.

Transmission electron microscope studies of this technique have shown that the additional delta layer grown by MBE is indistinguishable from the original lattice and that there are very small density of defects at the substrate-epilayer interface or the delta layer.[7] Note that, unlike ion implantation, no annealing is performed on the lattice after the MBE process to incorporate the boron in the lattice or remove damage. Deposition of Si is performed by electron beam evaporation, which produces potentially damaging x rays. However, the total x-ray dose received during the MBE modification of the CCD is about 6 krad, which is significantly below the damage threshold of the device. Measurements on the dark current and CTE have shown that the delta-doped CCD exhibits the same characteristics as a typical Reticon 512x512 CCD of this grade and that there is no evidence of damage to the CCD. If necessary, electron beam evaporation can be replaced by thermal evaporation of silicon to avoid exposure of the CCDS to x rays.

5. Summary

Delta-doped CCD technology enhances the UV response of thinned, backside-illuminated CCDS by using MBE to incorporate 30% of a monolayer of boron atoms 5 Å below the backside silicon crystal surface. With this technique, backside potential well is effectively eliminated, yielding devices with 100% internal quantum efficiency in the near UV and blue visible. The response of delta-doped CCDS is highly uniform and these devices have exhibited long-term stability. The measured quantum efficiency of the CCD is mainly limited by the reflection of incident photons from the Si surface. Enhancement of the total quantum efficiency with antireflection coatings has been demonstrated by depositing HfO_2 on a delta-doped CCD for the wavelength range of 250-400 nrn.

6. Acknowledgment

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