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OXIDE DEGRADATION EFFECTS IN DRY PATTERNING OF RESIST USING NEUTRAL OXYGEN BEAMS

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ABSTRACT

Novel processing methods are being studied to address the highly selective and directional etch requirements of the ULSI manufacturing era; neutral molecular and atomic beams are two promising candidates. In this study, the potential of 5 eV neutral atomic oxygen beams for dry development of photoresist is demonstrated for application in patterning of CMOS devices. The patterning of photoresist directly on polysilicon gate layers enables the use of a self-contained dry processing strategy, with oxygen beams for resist etching and chlorine beams for polysilicon etching. Exposure to such reactive low-energy species and to the UV radiation from the line-of-sight, high-density plasma source can, however, alter MOSFET gate oxide quality, impacting device performance and reliability. We have studied this processing related device integrity issue by subjecting polysilicon gate MOS structures to exposure treatments similar to those used in resist patterning using low energy (5-20 eV) oxygen beams. Electrical C-V characterization shows a significant increase in the oxide trapped charge (30-90x) and interface state density(30-60x) upon low energy exposure. I-V and dielectric breakdown characterization show increased low-field leakage characteristics for the same exposure. High-field electron injection studies reveal that the 0.25-V to 0.5-V negative flatband shifts (measured after oxygen beam exposure) can be partially annealed by the carrier injection. This could be due to positive charge annihilation or electron trapping, or some combination of both. Physical analysis of patterned resist layers and electrical characterization data of MOS structures exposed to different neutral bam processing environments and following thermal annealing treatments is presented.

INTRODUCTION

The search for highly selective and directional etch processes for semiconductor manufacturing has prompted investigations of neutral atomic and molecular beams. The etching of materials such as Pb, GaAs, and Si has been reported by the use of heated jets of halogen containing compounds [1,2]. These heated jets produce atomic dissociation products which are very reactive and can anisotropically etch various materials of interest in semiconductor manufacture, particularly silicon. Silicon can be etched by either heated SF_6 [3] or heated Cl_2 [4] beams. A selectivity of 1000:1 over silicon dioxide has been seen [4] with high aniso-

tropy. The low energy range (< 10 eV) of these netural beams compared with that of plasma processes (> 15 eV) makes them attractive for applications where high selectivity is required, such as in polysilicon gate etching or photoresist development [5]. Low energy beams promise appear to be an attractive alternative to plasma techniques [4]. ?

The goal of this study is to investigate the feasibility of using neutralized species extracted from a plasma to etch photoresist. The patterning of photoresist directly on polysilicon gate structures offers the possiblity of a completely self contained dry process using oxygen to etch resist and chlorine to etch polysilicon. The feasibility of using hot molecular chlorine to etch polysilicon has already been reported [4]. The dry development of silylated photoresist requires a selective etch process to remove organic material in specific regions with high selectivity to other areas which contain a diffused inorganic such as silicon dioxide. This is commonly done by using a oxygen plasma. We report the first use of a neutralized oxygen beam to accomplish the development step of a dry developable resist.

The dry etching of organic materials forms the basis of various pattern transfer schemes in semiconductor manufacturing technology [5]. One scheme, known as multilayer lithography, relies on exposing a thin imaging resist and transfering that image into a thin inorganic layer followed by a thicker organic layer. In another technique, known as surface imaging, a thick resist is exposed only in the top portion. Development is accomplished by preferential diffusion of an unetchable material (organosilane) into exposed areas(for a negative tone resist). The diffused regions are resistant to etching in an oxygen plasma, thus forming the basis of a dry developable resist system [6]. The best known of these is the commercially available DESIRE system [7].

Dry etching of these resists relies on an inorganic barrier or silylated region to effectively mask the underlying organic material during an oxygen plasma treatment. In the case of dry developable resists, the silicon containing mask must form a continuous barrier layer during the etch, free of pinholes or other defects. The etch must be highly selective to the silicon containing region, removing resist only in unsilylated areas. Also, etching must be anisotropic to obtain vertical profiles in the resist. Neutral beams may be a attractive alternatives to plasma techniques. The goal of this study was to see if the neutral atomic oxygen beam could be used to selectively etch silylated resist patterns with minimal damage to device structures.

This work investigates the potential degradation in MOS characteristics due to the resist etch process practiced here. Damage can occur because of physical bombardment of atoms directly over the gate, and/or sample exposure to UV radiation (193 nm) generated in the plasma source. The latter possibility is common to all neutral beam source configurations within line-of-sight of a plasma.

EXPERIMENT

The silylated resist experiments here were done on the negative tone Poly - 4 - (tert - butlyoxycarbonyloxy) - styrene (PBOCST)-based dry develop system which is a variation on the system developed at IBM Almaden [8,9]. This photoresist was spin-coated on 125 mm silicon wafers to achieve a 1.2 micron thick film, pattern exposed, then silylated with dimethly-amino-trimethylsilane(DMATMS). Wafers were split into quarters for etching in the atomic oxygen beam. Following etching, cross sections or resist samples were taken and examined by scanning electron microscopy for resist profile.

Etching was performed at the atomic oxygen beam source developed at the Princeton Plasma Physics Lab for NASA investigations of low Earth orbit vehicles. This source was previously used to study the erosion of organic materials for spacecraft applications [11] and produces an atomic oxygen beam with energies of 5-10 eV. The neutral source is based on the surface neutralization of a lower hybrid plasma source [12]. The current configuration has a duty cycle of 10% and produces an atomic oxygen flux of approximately $5x10^{16}/cm^2$-sec with an average energy of 5 eV +/- 4 eV. Samples were exposed from 1 to 5 h. to achieve a dose equivalent to that required to etch approximitely 1 micron thick photoresist.

MOS capacitors for the damage measurements were fabricated on 125 mm diameter p-Si<100> wafers. A 10-nm thermal gate oxide layer was grown in 5000 Å recessed oxide (ROX) isolated regions. A 3000 Å thick boron-doped polysilicon plate formed the gate electrode. A dry polysilicon etch procedure was employed to define individual capacitors. A 30 min. 400 °C forming gas anneal followed back-side Al metallization. Devices were directly exposed to the neutral beam environment; a combination of exposure time (0-5 h) and oxygen beam energy (5-20 eV) defined the experimental splits. Control samples received no exposure. Electrical characterization involved standard MOS capacitance-voltage (CV), current-voltage (IV), and Fowler-Nordheim tunneling injection stressing measurements [13].

RESULTS AND DISCUSSION

Figure 1 shows a schematic of apparatus and the resulting SEM photographs of surface-imaged resists after exposure to the atomic oxygen beam. The three photographs were exposed at different locations with respect to the beam axis, illustrating the effect of beam divergence on the profiles. The sidewall slopes for samples exposed on beamline appear symmetric and nearly vertical, indicating that the atomic oxygen beam etch is highly anisotropic. The far slopes illustrate the shadowing effect of the beam caused by the structure being etched. The inner slopes are representative of the divergence of the beam, which is estimated to be about 5-10 degrees.

Figure 2 shows a comparison of SEM photographs of 1 micron lines and spaces in resist developed in both plasma and neutral-beam environments. The top two photographs were developed in plasmas, the bottom in the neutral-beam. The top photograph illustrates the undercut seen in a standard, magnetically enhanced parallel plate plasma etcher. The middle photograph is of ECR plasma- etched resist and the bottom photograph, neutral-beam etched (close to axis). Both the ECR and the neutral-beam profiles show promising anisotropy.

Electrical CV and IV measurements on control samples showed high quality MOS characteristics. MOS flatband ($V_{fb}=0.25$ V), midgap density of interface states (D_{it}) = 1.1×10^{10} $eV^{-1}cm^{-2}$, and oxide breakdown voltage (≈ 16 V), were measured. However, neutral beam exposure resulted in significant degradation in MOS characteristics.

Figure 3 shows IV data for four different sample conditions. Neutral oxygen-beam exposure results in three major changes to the IV characteristics. First, the tunneling component of the leakage current sets in at lower voltages and is independent of the exposure conditions. Second, the intrinsic breakdown of the exposed devices occurs at lower voltages (Figure 3 shows the exception), and finally, for certain preoxidation cleaning conditions, a 5 h, 20 eV exposure results in the formation of oxide traps and the IV characteristics become significantly distorted (see Figure 3). Exposure also results in the formation of trapped positive charge and interface states, thereby altering the CV characteristics. Exposures result in flat-band shifts of -0.3 to -0.5 V, and an increase in the density of interface traps of 10-15X.

Exposure also modulated the reliability characteristics of the MOS structures. Figure 4 shows MOS V_{fb} plotted as a function of Fowler-Nordheim High Field Injection (HFI) dose. The data illustrates that neutral beam exposures generated the trapped charge. HFI carriers, while transported across the oxide layer of the exposed samples, neutralize some of the positive trapped charge, thereby shifting the MOS V_{fb} in a positive direction. Since the neutralization is only partial, the recovery in MOS V_{fb} does not proceed to the pre-exposure value. HFI of the control samples provide a different response. Because the level of trapped charge in the clean oxide is minimal, HFI carriers do not participate in any neutralization process, but instead cause some oxide damage by bond breaking. Hence, HFI of the control samples results in a gradual negative shift in the MOS V_{fb} as injection proceeds.

All exposure-related MOS degradation effects were removable by a low-temperature, post-exposure forming gas (30 min., 400 °C) procedure. HFI-induced characteristics were also reversible to those of the control samples. Both the nature of damage introduced by the neutral-beam exposure and the ability to anneal the oxide damage suggests that neutral-beam related damage is primarily caused by exposure to UV radiation. It is well known that UV and x-ray irradiated MOS devices exhibit degradation and annealing behavior that are similar to the samples in this study [14]. This presentation discusses details of the electrical measurements.

CONCLUSIONS

The feasiblility of neutral oxygen-beam patterning of dry develop photoresist has been demonstrated, illustrating the high anistropy and selectivity possible with a 5 eV beam. Profiles obtained in surface-imaged resist are similar to those obtained in an ECR plasma. Electrical CV and IV measurements show degradation of MOS capacitor structures as a result of neutral beam exposure. However, this damage is annealable for the most part and is likely the result of UV exposure from the plasma region of the beam apparatus.

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FIGURES

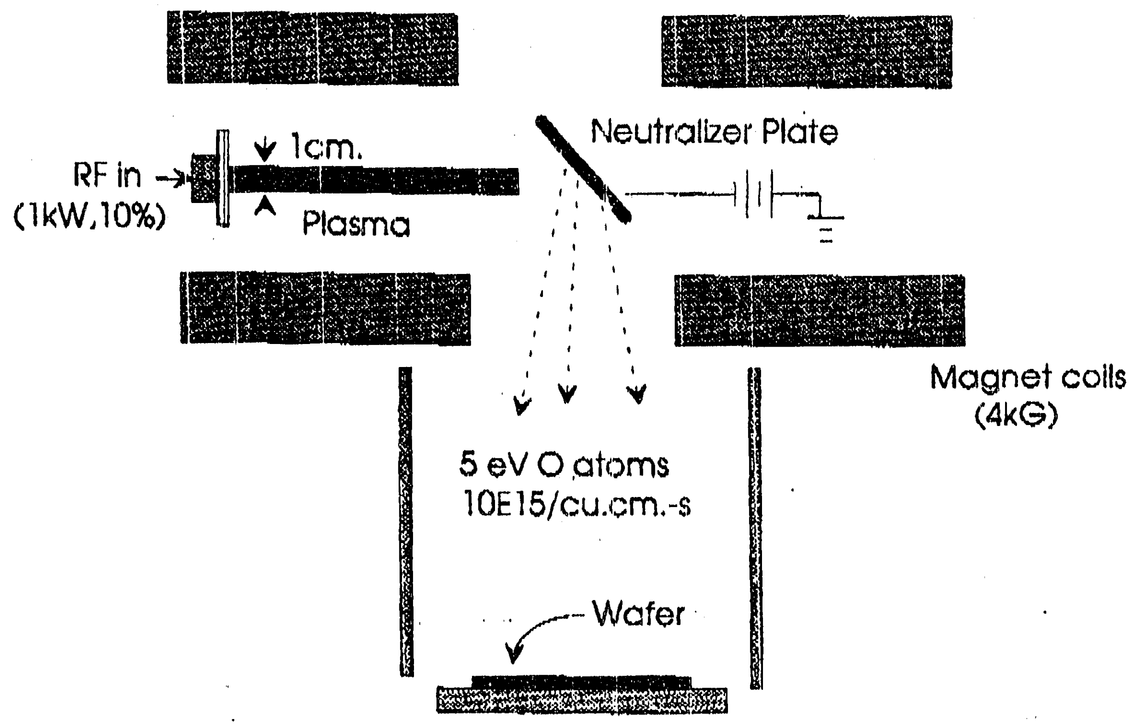
Figure 1: Schematic of the apparatus used for this experiment and the resulting SEM profiles in photoresist.

Figure 2: SEM photographs of tBOC resist etched in different systems; top: magnetically enhanced parallel- plate plasma system, middle: divergent ECR plasma, bottom: 5 eV neutral oxygen beam.

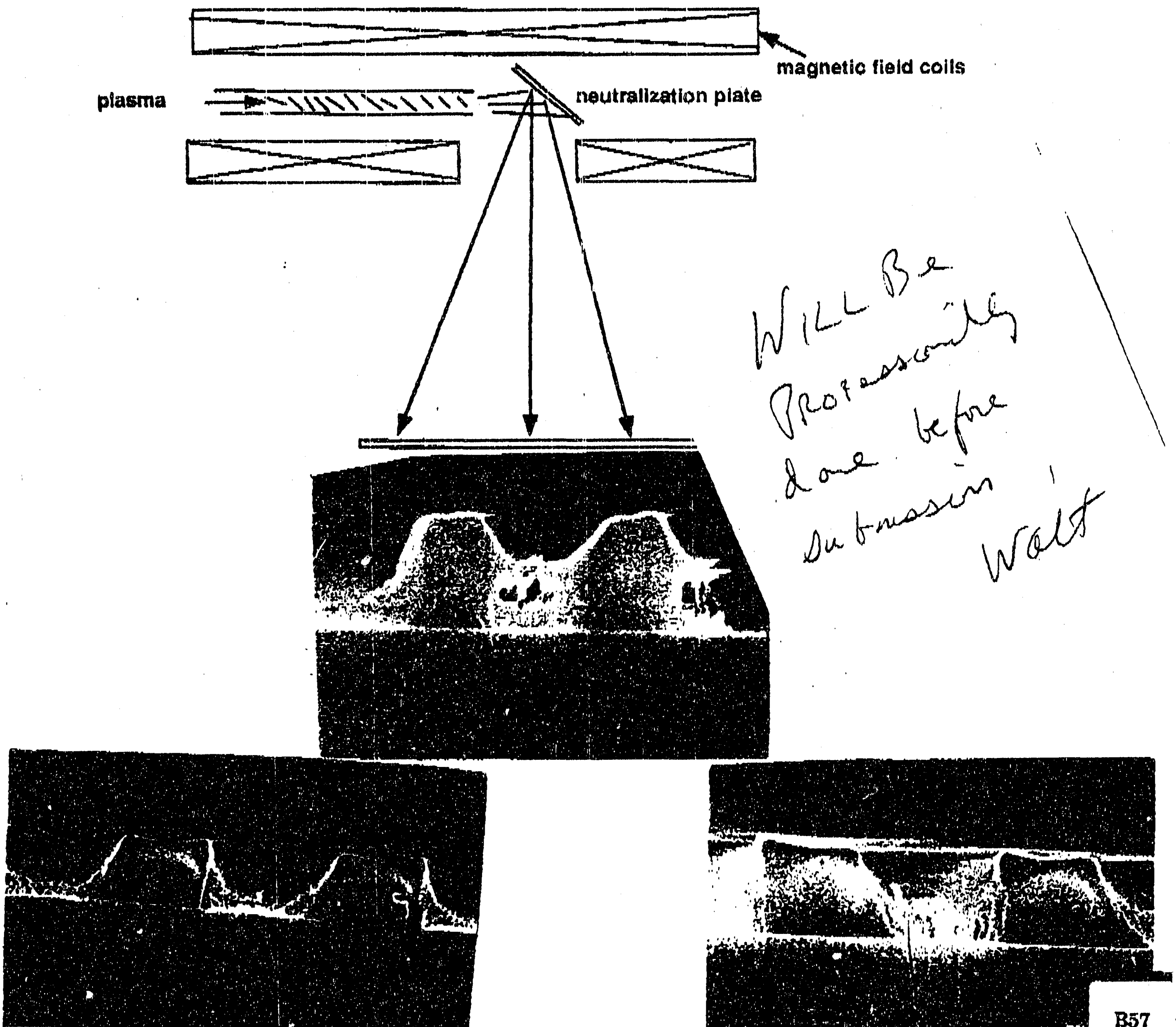
Figure 3: Current-Voltage (IV) characteristics of MOS capacitors exposed to low-energy neutral oxygen beams. Sample and measurement details are provided in the inset.

Figure 4: Plot of the changes in MOS V_{th} as a function of Fowler-Nordheim high-field injected charge dose. Data is shown for control and low-energy oxygen beam exposed MOS capacitors. Constant current injection was carried out for periods of 30 s. each between V_{th} measurements.

Neutral Beam Apparatus



Neutral Beam Apparatus



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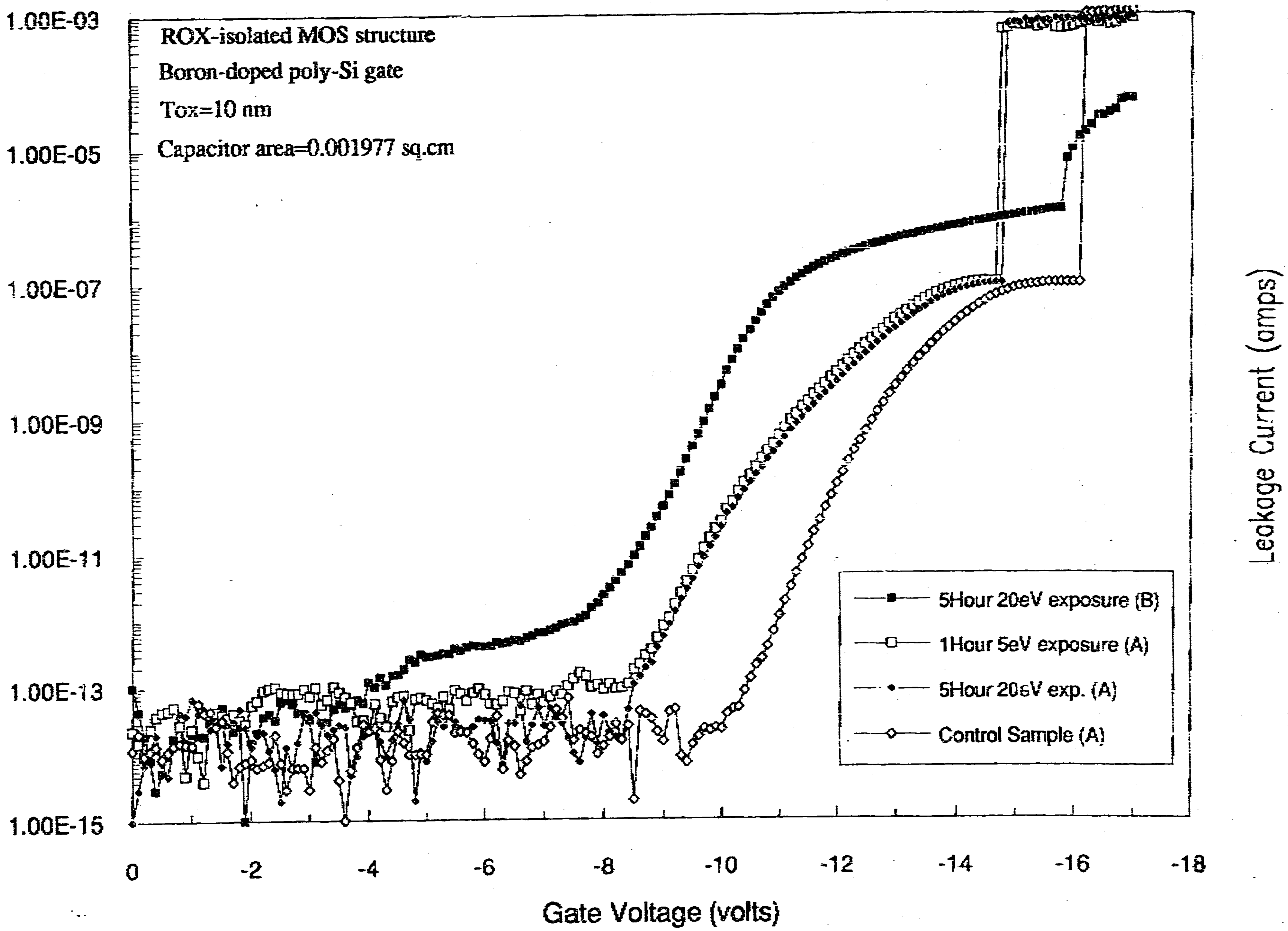
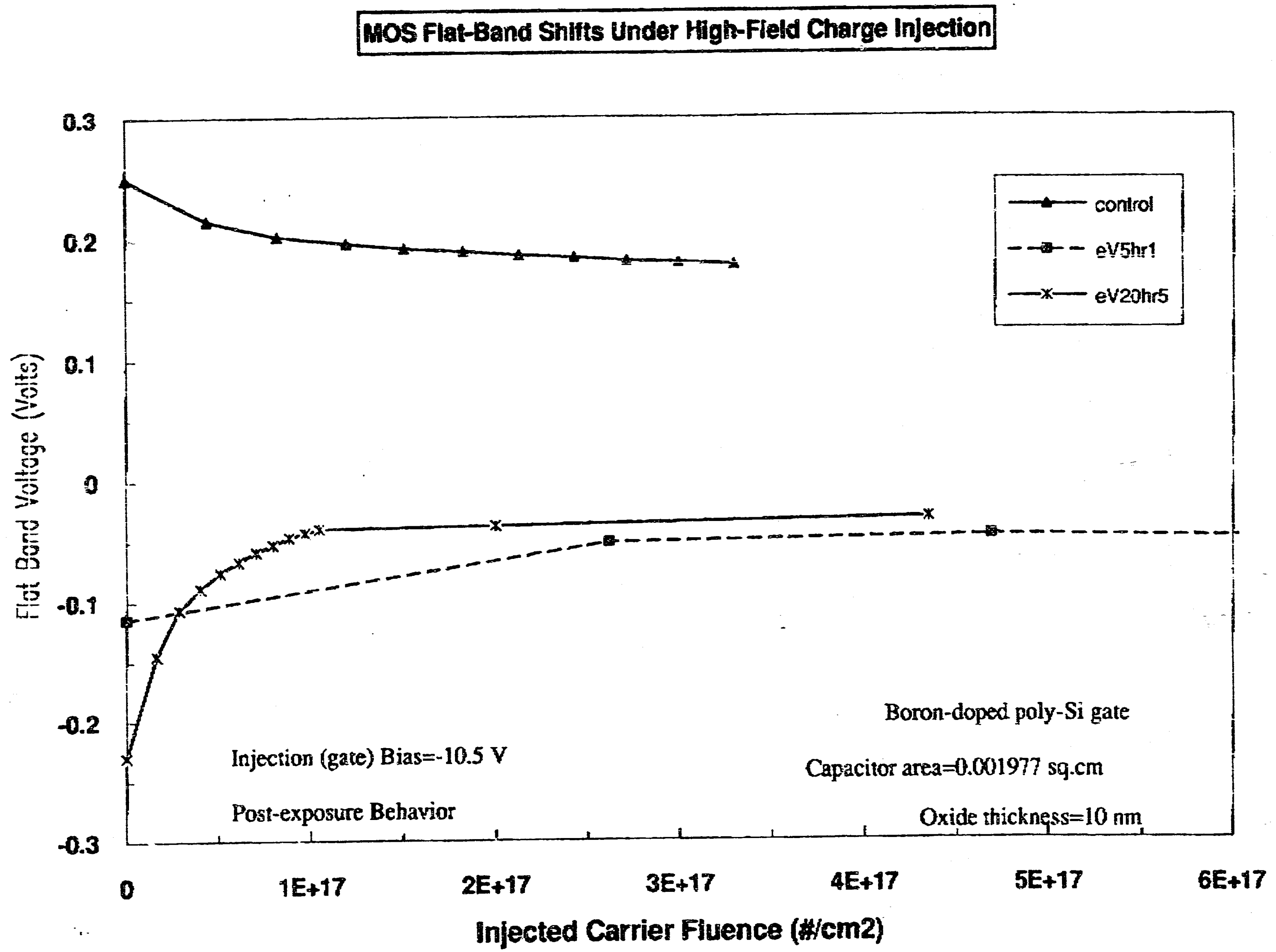
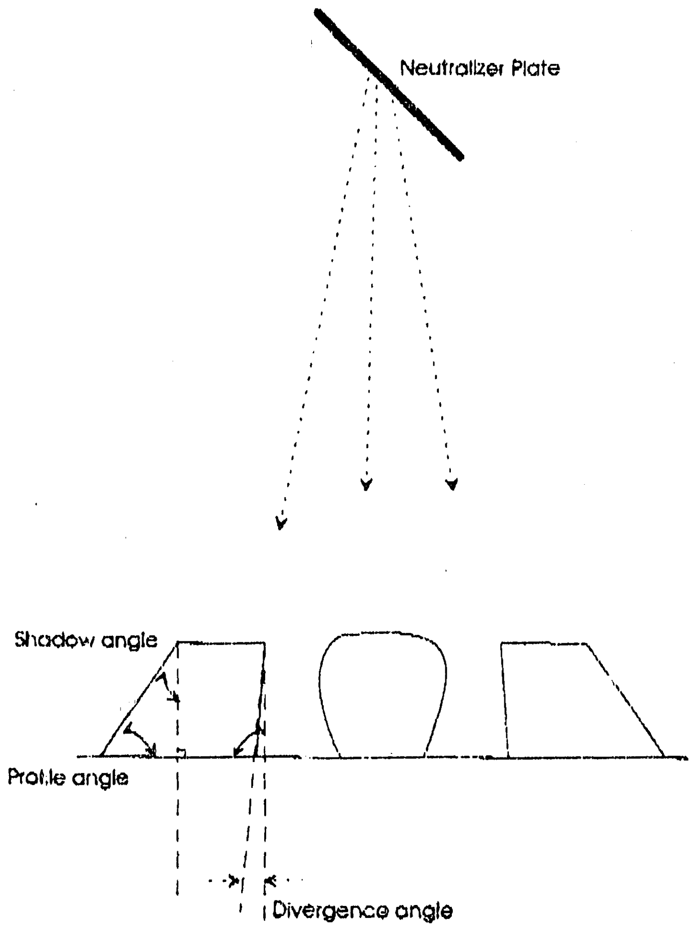
(Fig. 3)


ROX-isolated MOS structure
Boron-doped poly-Si gate
Tox=10 nm
Capacitor area=0.001977 sq.cm
1.00E-03
1.00E-05
1.00E-07
1.00E-09
1.00E-11
1.00E-13
1.00E-15
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
Gate Voltage (volts)
Leakage Current (amps)
5Hour 20eV exposure (B)
1Hour 5eV exposure (A)
5Hour 20eV exp. (A)
Control Sample (A)

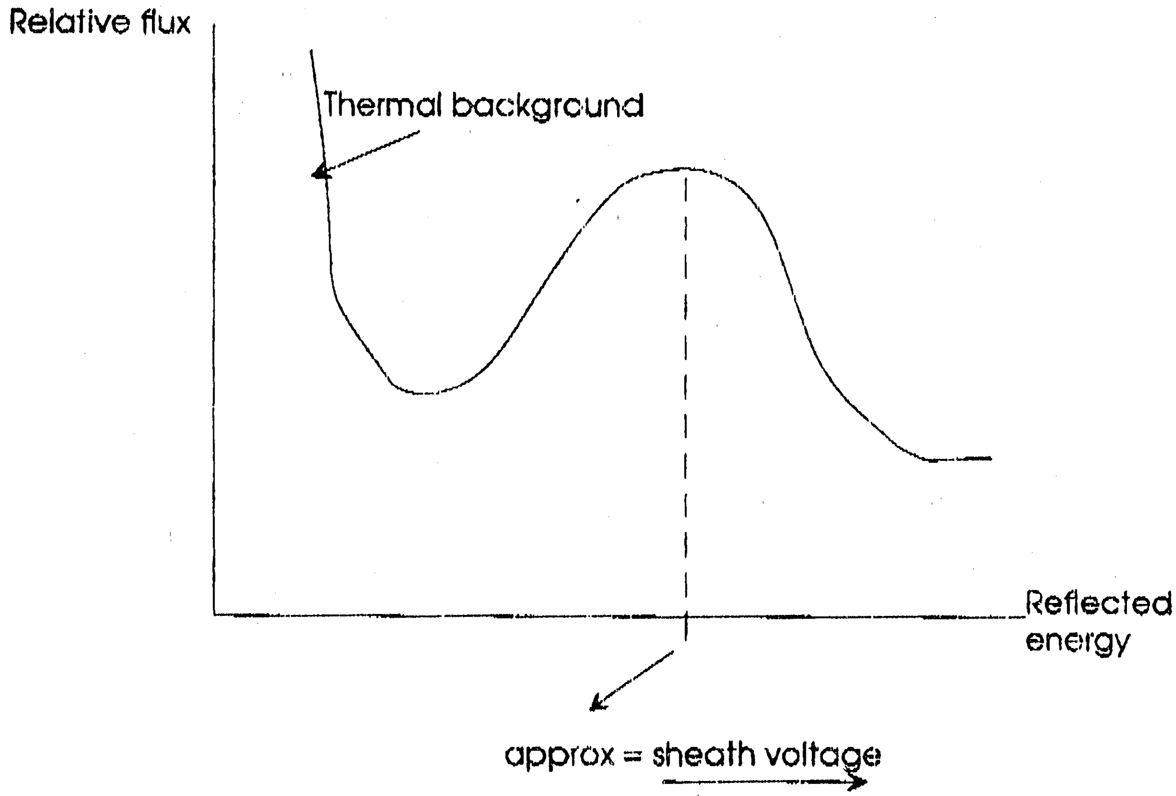
(Fig. 4)


MOS Flat-Band Shifts Under High-Field Charge Injection
control
eV5hr1
eV20hr5
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
Flat Band Voltage (Volts)
0
1E+17
2E+17
3E+17
4E+17
5E+17
6E+17
Injected Carrier Fluence (#/cm2)
Injection (gate) Bias=-10.5 V
Post-exposure Behavior
Boron-doped poly-Si gate
Capacitor area=0.001977 sq.cm
Oxide thickness=10 nm

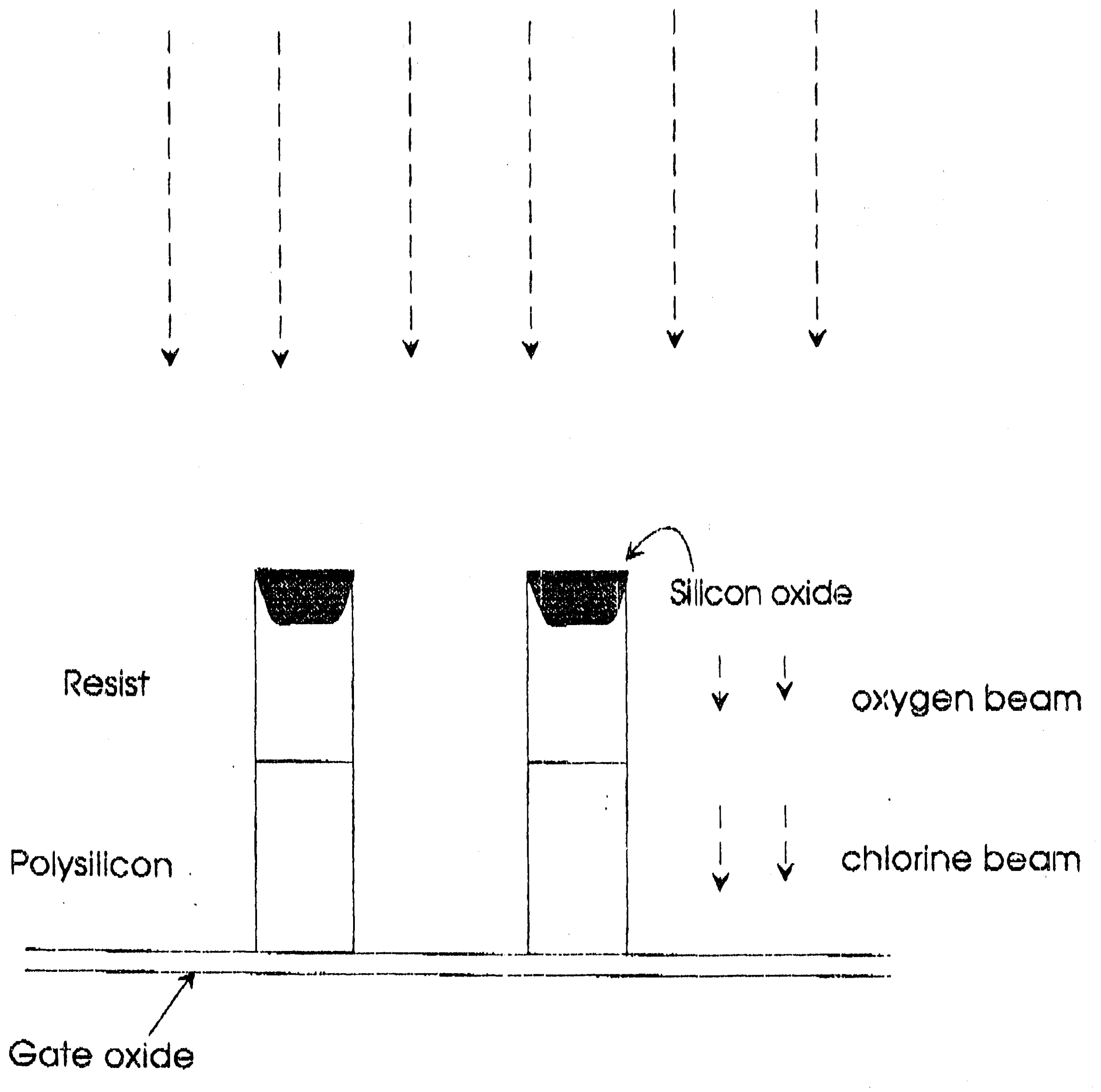
Effect of Divergence on Profiles



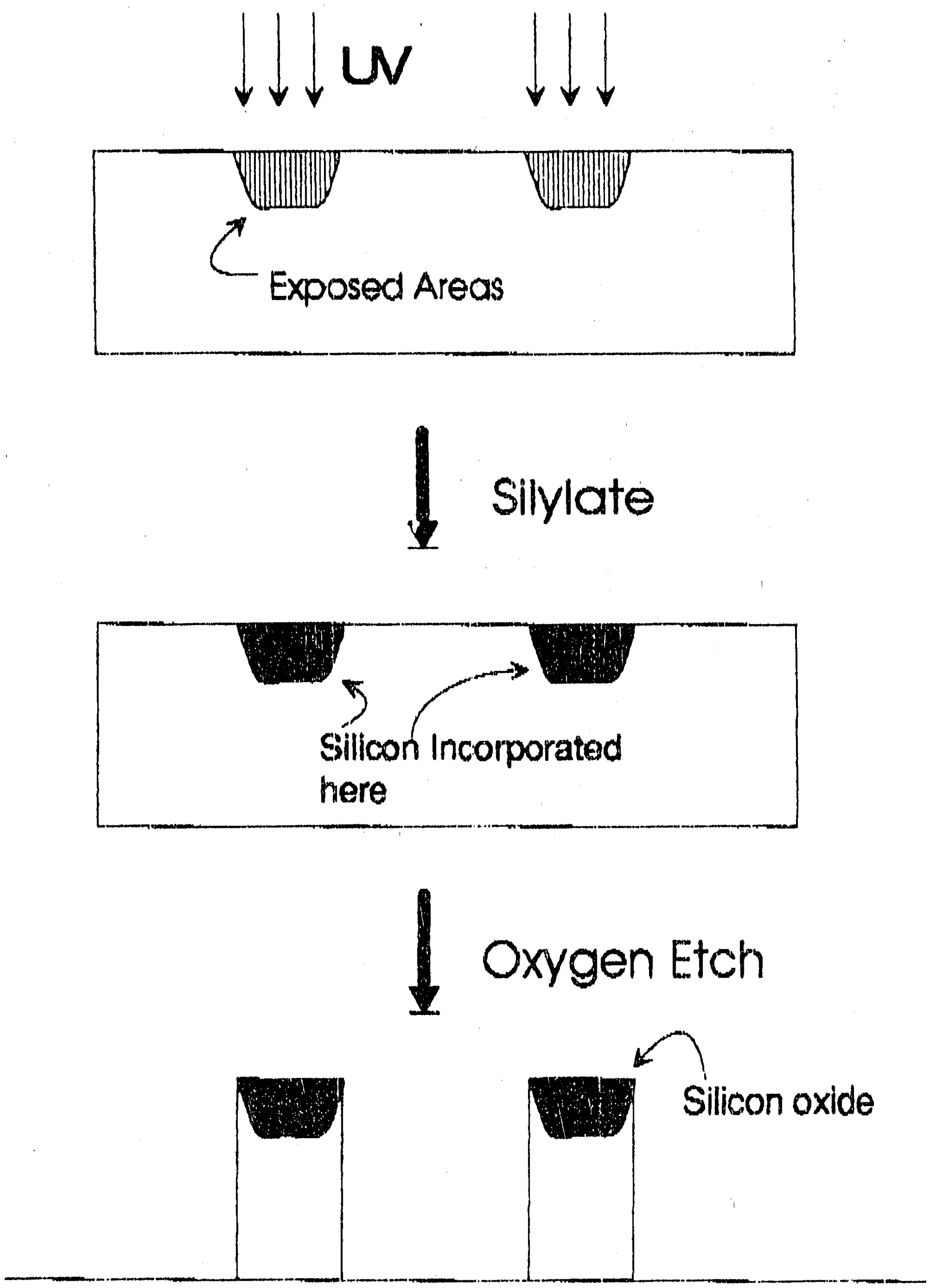
Ion Reflection and Neutralization



Motivation: Dry patterning of polysilicon gates



Dry Resist Development



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