

Photoresist Strip Challenges for Advanced Lithography at 20nm Technology Node and Beyond

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ABSTRACT

Photoresist strip has traditionally been a low technology process step, but is becoming increasingly more complex with the migration to ultra-shallow junctions, 3D structures, double patterning, and high-mobility channels. At junction depths of a few tens of nanometers, surface effects become increasingly important. Small changes to surface conditions can affect junction resistivity, junction depth, and dopant activation.

Advanced high-resolution chemically amplified resist can be problematic when used as an implant mask. Ion beam induced chain scission and photoacid generation can lead to thermal instabilities during the resist strip process. Multi-level resist structures can be difficult to remove and rework and high aspect ratio 3D structures can require near infinite selectivity during the strip processes. This paper will summarize the issues and offer options for solutions.

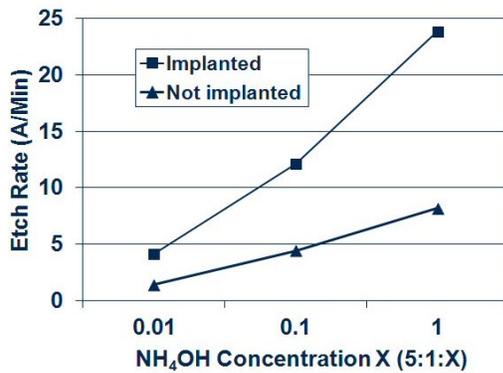
Keywords: Photoresist, Strip, Ash, Dopant Retention, Dopant Loss, Junction Recess, Ion Implantation, Hard Mask, Substrate Loss, Substrate Oxidation.

1. INTRODUCTION

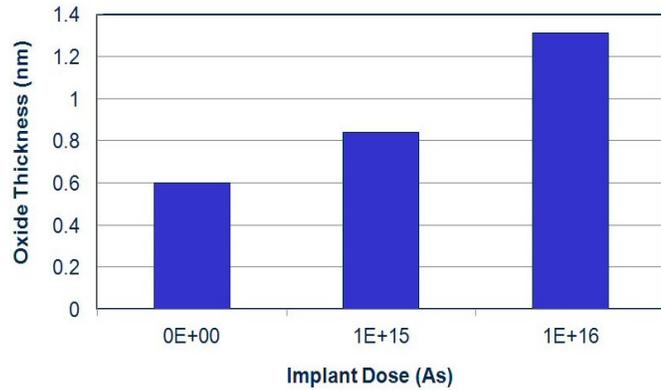
Traditionally, photoresist stacks were purely organic layers patterned over purely inorganic materials. Oxygen based plasmas removed the organic material with near infinite selectivity to the underlying layers. Any remaining residues could then be removed in standard aqueous cleaning chemistries such as SPM + APM or RCA (SC1 + SC2) cleans. The migration to double patterning, immersion, and multi-layer resist stacks containing silicon or other inorganic elements combined with substrates that are sensitive to oxidation, place constraints on the photoresist removal and subsequent wafer cleaning. New substrate materials such as SiGe and III-V materials are readily oxidized requiring non-oxidizing strip processes [1,2]. Hydrogen based strip plasmas have been used to eliminate substrate oxidation, but these processes have issues of their own, such as dopant deactivation, hydrogen vacancy enhanced oxidation and process chamber contamination [3]. Solutions are only now emerging to these and other issues.

2. SUBSTRATE AND JUNCTION OXIDATION AND ETCHING

Plasma oxidation of source/drain junctions and junction extensions in silicon, silicon-germanium, and other substrates has become an issue for photoresist strip. This is especially true for ultra-shallow junctions and doping of FinFET devices [4]. As a further complication, the ion damage substantially increases the substrate attack and etch rate [5,6]. Figure 1(a) demonstrates the effect of implant damage on the enhancement of silicon etch rate from standard SC1 [7] wafer cleans. Typical etch rate enhancements increase by factors of 4 or more. Similar enhancement effects are seen for BOE and dilute HF cleans [6]. For plasma striping the implantation damage enhances the oxidation of silicon as seen in Figure 1(b). It has been repeatedly shown that this enhancement in etch rate and oxidation rate correlates with the degree of ion damage and is somewhat independent of implanted ion species [5,6].



(a)



(b)

Figure 1a. Silicon etch rate in SC1 as a function of the NH₄OH concentration (by volume) for non-implanted silicon and 5x10¹⁵ ions/cm² Arsenic implanted silicon (un-annealed)

Figure 1b. Increase in silicon surface oxide thickness after 90%O₂ + 10%FG (forming gas) plasma exposure for 3 minutes at 250C versus arsenic ion implant dose at 3keV

The amorphization layer generated by the ion implantation is highly reactive and easily oxidized by the plasma or other post process steps. For common oxygen plasma exposures this the entire amorphous layer will have a high background oxygen level. This enhanced oxidation will lead to increases in junction recess and cause dopant loss and increased junction series resistance.

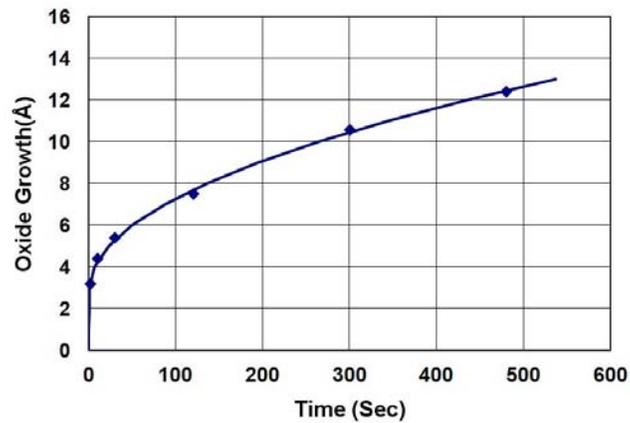


Figure 2. Plasma Oxidation Growth at 250°C for an O₂+10%FG plasma. The growth is parabolic in thickness.

Studies of the diffusion kinetics also show that oxidation is dramatically increased in the presence of electric fields, through a field enhanced diffusion process. In the absence of fields, oxidation follows a Deal-Grove parabolic oxidation rate [8,9,10] and is on the order of 5-10Å for a typical oxygen based strip owing to the fast diffusion of oxygen atoms through the growing oxide. Figure 2 plots the parabolic growth rate of silicon oxide in the presence of an oxygen plasma at 250C. The oxidation of shallow junction regions increases the off-state leakage and increases series resistance [11,12], and is particularly damaging for 3D transistors. Figure 3 shows the change in a FinFET device performance when the strip and clean process oxidizes the extension doping as compared to a non-oxidizing strip process.

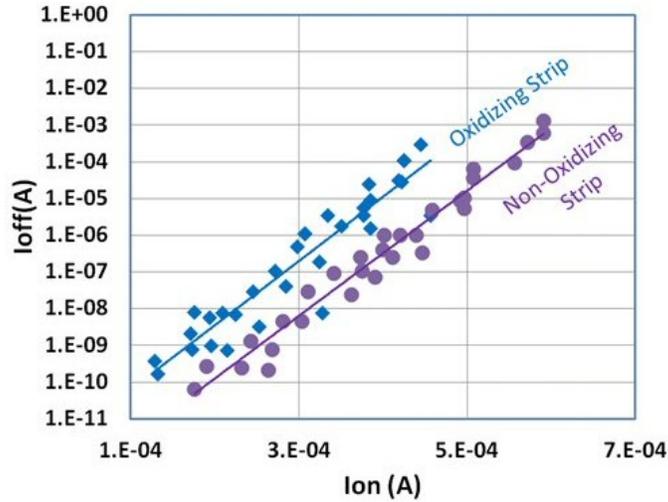


Figure 3. Ion – Ioff curve for a 20nm FinFET, comparing the performance of an oxidizing vs a non-oxidizing resist strip and clean. Oxidation of the extension region increases the series resistance and increases device leakage.

To eliminate oxidation effects, plasma strip processes based on hydrogen process chemistries (such as mixtures of N_2 and H_2) are being employed. Hydrogen processes however cause device shifts due to vacancy formation deep inside silicon and silicon-germanium substrates; see Section 3. Additionally hydrogen based plasmas do not convert the photoresist into gaseous by-products, but instead crack the resist polymer into shorter-chain organics which can condense onto chamber walls, pumping lines and exhaust lines causing particle issues and potential fire hazards. Shown in Figure 4 is a condition where the pumping line was inspected after 1000 wafers coated with $1.8\mu m$ of photoresist were plasma stripped in a plasma of forming gas (FG) versus stripping in a plasma of O_2+FG . (The FG was a mixture of 4% H_2 in N_2 .) Additionally an oily substance from the FG strip process was found condensed in the exhaust lines.



Figure 4. Example of cracked photoresist deposits in the vacuum line of a system running 1000 photoresist coated wafers using a forming gas (FG) plasma strip process (a) versus a system running an O_2+FG process (b). The FG process is a mixture of 4% H_2 in N_2 .

3. RESIST STRIP EFFECTS ON DOPANTS

At junction depths of several hundred angstroms or less, surface effects begin to make measureable and sometimes dramatic changes to the dopant profiles, junction depth, dopant activation and resultant resistivity. Significant changes to junction characteristics are observed when the near surface contains nitrogen or oxygen bonds prior to anneal [13,14].

Since the near surface can be significantly altered by the strip processes used, device shifts have been observed as a function of the strip process which caused changes in dopant placement and activation [15]. Nitrogen bonding for example acts as a vacancy source and as an interstitial trap. This produces a net increase in vacancies and a reduction of interstitials thereby enhancing n-type dopant diffusion (a vacancy diffuser), while retarding boron diffusion (an interstitial diffuser). Oxygen bonding conversely act as an interstitial source and vacancy trap. As a result oxygenated surfaces enhance boron diffusion and retard n-type dopant diffusion.

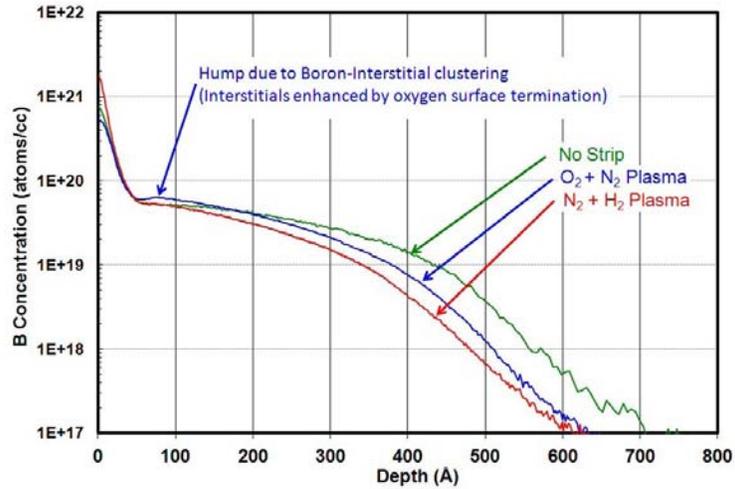


Figure 5. Secondary Ion Mass Spectrograph of a 600eV Boron implant subject to 2 different strip plasmas prior to anneal. After 1000C anneal for 30 seconds, significant changes to the annealed profile occur because of the plasma strip exposure. The results are consistent with similar observations made for wet clean surface terminations, namely nitrogen traps interstitials and injects vacancies, oxygen conversely traps vacancies and injects interstitials.

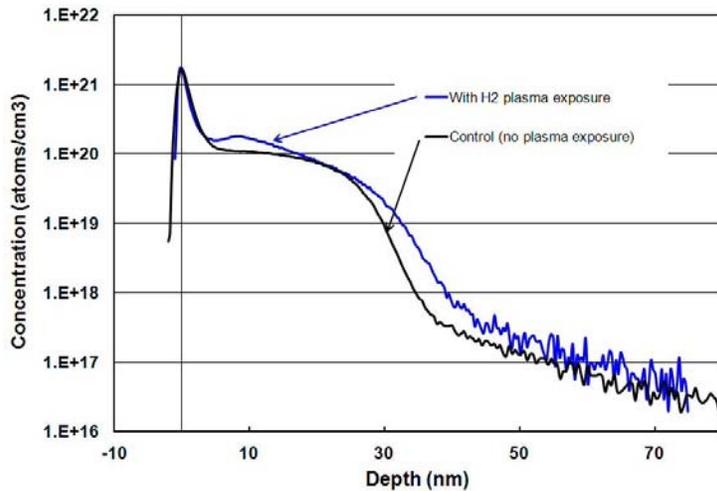


Figure 6. Secondary Ion mass Spectrograph of a 3keV Arsenic implant subject to a hydrogen based strip plasma prior to anneal. After 1000C anneal for 30 seconds, significant enhanced arsenic diffusion is observed for the hydrogen plasma condition. This enhanced diffusion is believed to be caused by TED from the vacancies formed deep in the silicon by the hydrogen exposure.

An example of this is shown in Figure 5 where a 600eV Boron Implant was exposed to different plasma strip chemistries prior to anneal. Clearly the FG plasma results in a shallower junction depth as compared to the no-strip case, as nitrogen acts as an interstitial trap reducing near surface interstitial density. The oxygen plus nitrogen process shows effects of interstitial injection due to oxygen termination as seen by the hump in the profile at about 80Å depth indicative of an effect known as Boron-Interstitial clustering [16,17]. The reduced diffusion length in this case is caused by the nitrogen interstitial trapping. These strip effects are clearly seen in device performance, and significant device shifts can be observed as a function of photoresist strip chemistry [15]. It has also been observed that plasmas containing even small amounts of fluorine can preferentially bleach out boron from the damaged crystalline lattice [15].

Hydrogen also has shown the ability to alter dopant profiles [18]. Hydrogen penetrates deep into the silicon causing deep silicon vacancies. Because these vacancies are deep (not just surface effects), they contribute significantly to n-type dopant diffusion and dopant deactivation through Transient Enhanced Diffusion (TED) and dopant-vacancy clustering.

Figure 6 is an example of an arsenic implant that was exposed to hydrogen plasma prior to anneal. The silicon vacancies formed by the hydrogen plasma contribute to increasing arsenic TED as evidenced by the increased diffusion length, and shows evidence of Arsenic-Vacancy clustering as seen by the hump in the profile at around 10nm depth. This vacancy formation also can lead to high substrate oxidation as these vacancies readily re-oxidize in subsequent process steps [3].

4. ION IMPLANTATION INTERACTIONS WITH PHOTORESISTS

Ion implantation into any organic material produces physical and chemical changes. Chain scission, cross-linking, photoacid generation, densification and stress, etc, all occur simultaneously as a result ion implantation into chemically amplified resists [19,20,21]. Figure 7 represents a study of the effects of cross-linking versus scission for PMMA subjected to different ions at different doses. During ion exposure, PMMA like other polymers undergoes both scission and cross-linking events. For heavy ions, like Arsenic and above, cross-linking dominates at all doses and energies. For light ions, at low dose there are more scission events than cross-linking events so there is a net reduction of molecular weight. However at successfully higher doses, the build-up of cross-linking events eventually swings to an increase in the molecular weight.

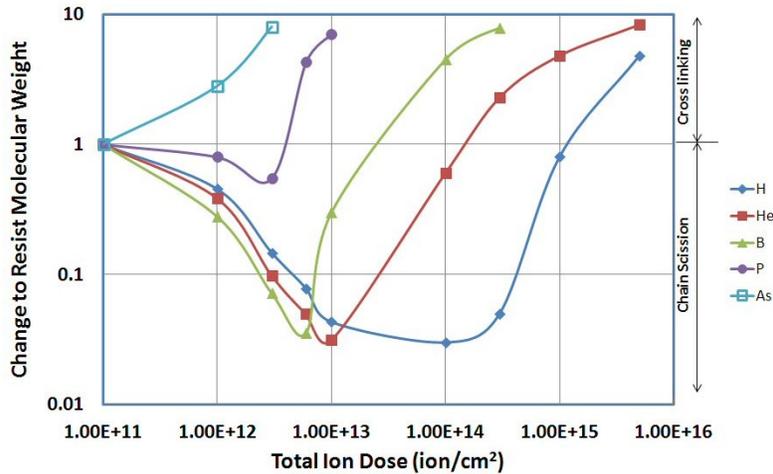


Figure 7. Relative change in molecular weight of poly(methyl methacrylate) (PMMA) after ion bombardment at different total ion doses.

Additionally the ion exposure can activate the photoactive groups in chemically activated resists. This activation through a deprotection reaction along with scission events reduces the thermal stability of the resist. Cross-linking conversely results in a thermally and chemically stable material with high carbon content. This cross-linked material, commonly called the implant “crust” has low chemical reactivity to resist removal chemistries.

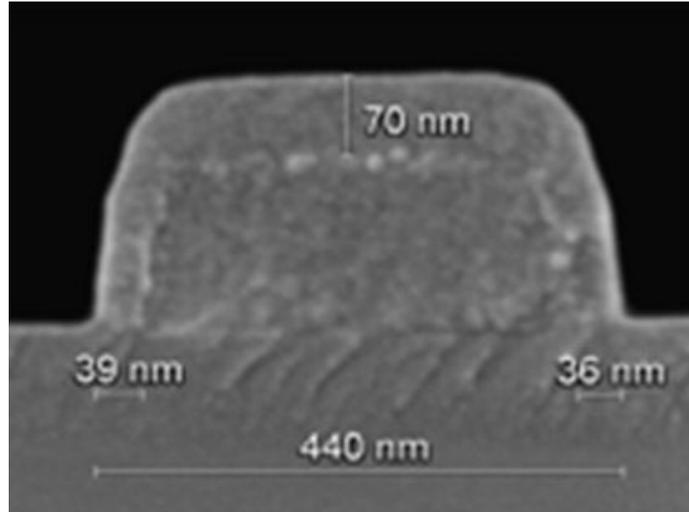


Figure 8. Typical cross-sectional SEM of a 193nm resist implanted with a typical source/drain extension implant.

Figure 8 is a typical cross-section of a 193nm resist line implanted with a typical source/drain implant. The cross-linked crust in this case is about 70nm thick. A region about 80nm down from the bottom of the crust is a layer with reduced molecular weight due to the scissions caused by the carbon co-implanted in this structure. Additionally the low-dose carbon has liberated photoacid from the photoactive groups (PAG). At elevated temperatures used for resist strip, the volatiles from the scission and deprotection reactions will cause pressure will build up inside the crust encapsulated resist structure, possibly resulting in resist popping.

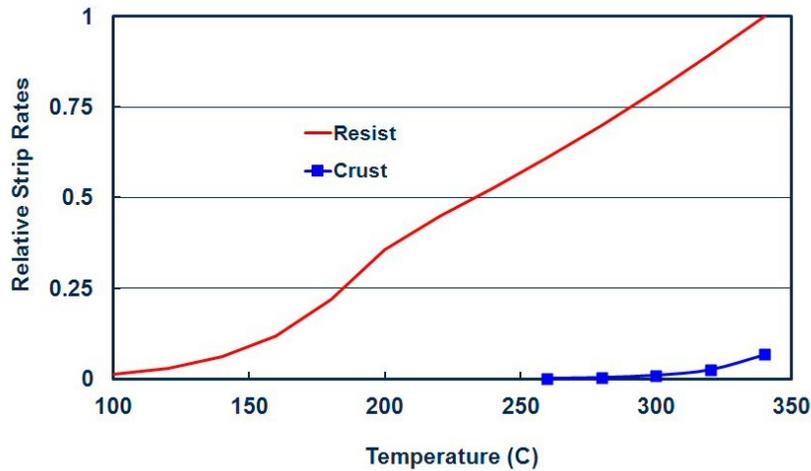


Figure 9. A comparison between the resist and crust removal rate for a 5×10^{15} Phosphorous implant into 248nm DUV resist utilizing an O_2 +FG plasma. (FG – forming gas). No measureable removal rate of the crosslinked crust region is observed at temperatures below about 300°C.

To remove the crosslinked crust effectively generally requires high temperatures since the chemical reaction between the plasma and the crust has very low reactivity (see Figure 9). It is estimated that the activation energy of the plasma reaction with the crust is about 2.6eV as compared to the activation energy with the photoresist of about 0.17eV [22].

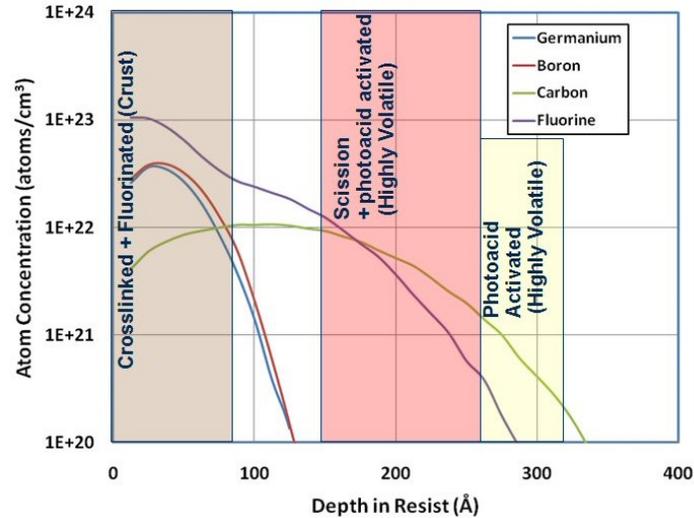


Figure 10. The ion implant profile in a photoresist that has been implanted with Germanium, BF_2 and Carbon. The low dose carbon causes scission and PAG activation deep into the resist, creating a volatile material encapsulated by the crust formed from the Germanium and Fluorine implant. Additionally the fluorine can cause the formation of CF bonding further reducing the chemical reactivity of the crust region.

Commonly the source, drain and extension implants are a mix of different implant species at different energies and doses. The resultant implanted structure is a complicated mix of different cross-linking, scission, and activated layers. A typical example is shown in Figure 10, where the implantation is a mixture of Ge - to amorphize the silicon, BF_2 - as a source of the Boron dopant, and C - to alter the boron diffusion kinetics. When such a structure is heated to temperatures necessary to remove the outer crust material, gases start evolving from the underlying (exposed) resist materials. The volatile materials then can explosively erupt causing what is commonly called resist “popping”. Figure 11 is a scanning electron microscope (SEM) image of similarly ion implanted deep-UV photoresist, when heated to 140C.

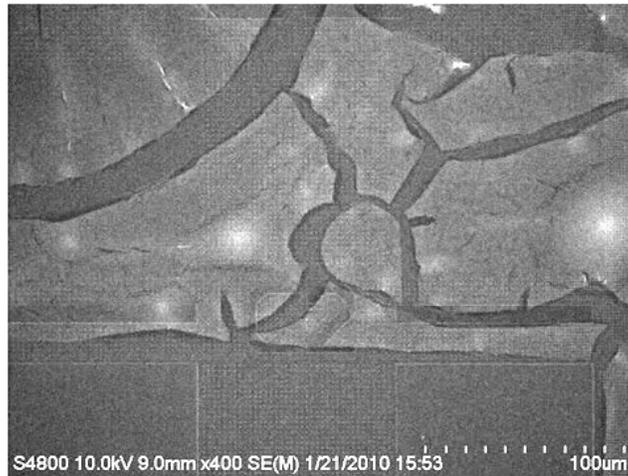


Figure 11. An implanted resist heated above the implanted resist’s popping temperature. Popping occurs when gases are evolved from thermal decomposition and deprotection reactions of the underlying resist and explode through the overlying crust.

The temperature at which an implanted resist pops is a function of many parameters including the Post-Exposure Bake (PEB) conditions, implant conditions, resist type, resist thickness, pattern density, and environmental conditions. Figure 12 demonstrates the environmental issues. In this study a 248nm DUV resist was implanted with arsenic and the

popping temperature was measured as a function of the time after the implant was performed. After more than 2 weeks of sitting in a cleanroom environment the popping temperature was dramatically reduced. The cause of this is believed to be due to moisture uptake, but other effects may also be occurring. It has been observed that chemically amplified resist exhibit a more pronounced delay effect and several fabs have imposed queue time limits between ion implantation and strip. Further study of this phenomenon is needed especially for immersion resists.



Figure 12. The measured popping temperature of a DUV photoresist as a function of the time delay after ion implantation. After about 2 weeks delay, the popping temperature is significantly reduced. For some resists, popping can be observed at room temperature after several weeks of sitting in cleanroom air.

The transition to normal incidence (zero degree) source/drain extension implants cause strong dependence on the strip characteristics of the resist and BARC/Underlayer sidewall profile. The photoresist strip challenges are magnified in the presence of footing or worse, undercut. For vertical or undercut resist sidewall profiles and zero degree implants, backspattering of substrate materials onto the resist sidewalls presents a difficult challenge for stripping [23].

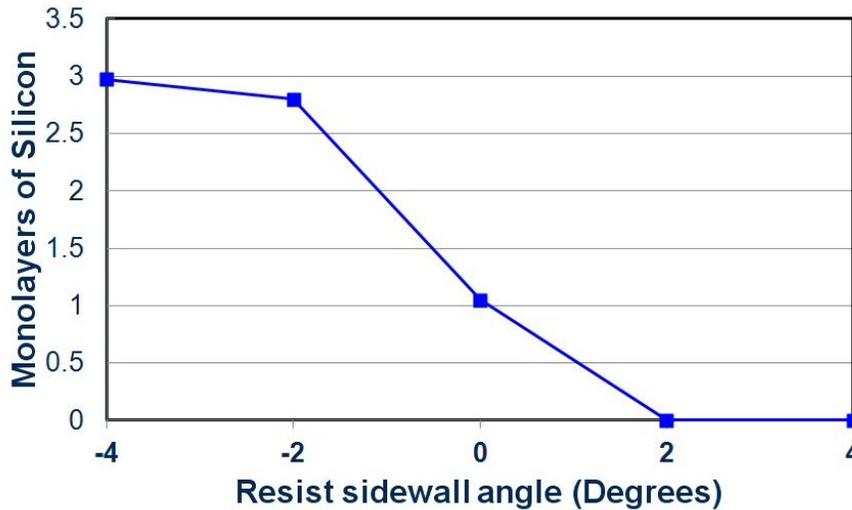


Figure 13. Monte-Carlo computer simulation of the amount of backspattered material (silicon) deposited on the sidewall of a resist mask during a normal incidence (0° implant) 5×10^{15} ions/cm² arsenic implant at 3keV and 5° beam divergence as a function of resist sidewall angle (negative values are for undercut).

Figure 13 is a computer simulation of the degree of backspattered substrate material (silicon) deposited onto the sidewall of a resist mask during a 3keV Arsenic implant at a total dose of 5×10^{15} ions/cm² for a zero degree implant angle, and

assuming a 1 sigma beam divergence of 5 degrees. For angled implants that were used in past generation technologies (typically 7°) the ion beam self-cleaned the resist sidewall due to glancing angle sputtering. For zero degree implants the self-cleaning effect is greatly reduced as the only significant ion cleaning comes from the beam divergence. As can be seen in Figure 13, at zero degrees and undercut profiles, significant backsputtered silicon can reside on the resist sidewalls. Removal of these silicon deposits require the use of a fluorine chemistry that can also etch junctions, bleach out dopants and increase junction recess [15].

5. REWORK OF MULTI-LAYER RESIST (MLR) STACKS

MLR rework presents unique challenges. Ideally it is preferred that each layer in the MLR structure can be removed with high selectivity to the layer immediately below it. For MLR structures that are all purely organic, this becomes a near impossibility. For MLR stacks including silicon containing hard masks or hardmasks containing amorphous carbon, reasonable selectivity can be achieved provided resist strip sensitive substrate materials are not exposed. For rework of the imaging layer, standard oxygen-based strip processes generally have issues with cracking and delamination of the hardmask because of the oxygen atom reactivity and permeability of most thin hardmask materials. An example of this delamination is seen in Figure 14 where the SiARC hardmask has cracked and delaminated from the underlying organic spin-on-mask material. This cracking and delamination can be avoided by utilizing non-oxidizing plasma strip chemistries to remove/rework the imaging layer.

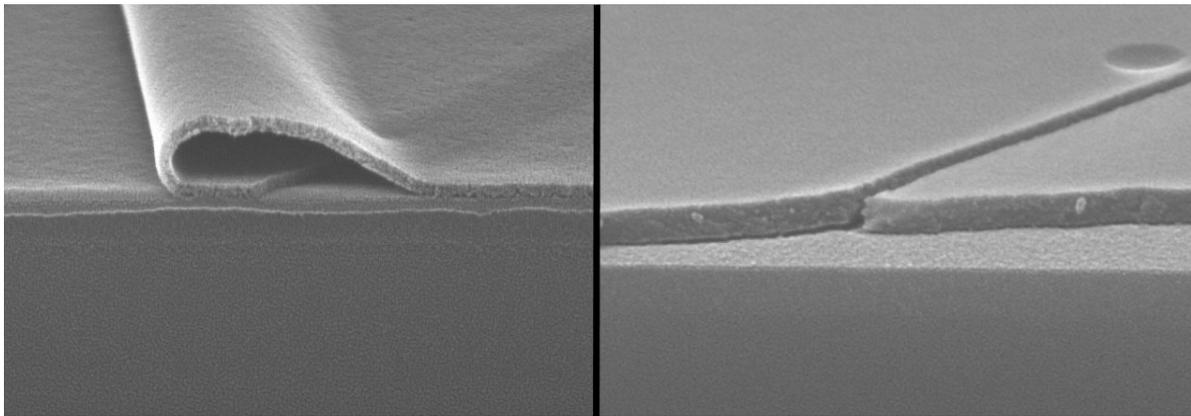


Figure 14. Cracking and delamination of a spin-on, silicon hardmask material (SiARC) after exposure to an oxygen plasma for 30 seconds at 245C.

6. RESIST STRIP OVER HIGH-ASPECT RATIO (HAR) STRUCTURES.

3D devices, DRAM storage cells, and STI are approaching or in many cases exceeding aspect ratios of 20:1. In advanced DRAM, the requirement to strip through a masking layer which is filling an HAR structure of up to 2µm deep while limiting the change to the cell electrode resistivity by no more than 5% is extremely difficult. To achieve this requires a selectivity of resist strip to TiN attack of greater than about 20,000:1. An example of this is seen in Figure 15. Use of a standard O₂+FG plasma would completely oxidize the TiN material before all the resist was removed.

In addition to high selectivity requirements, HAR structures are sensitive to hydrostatic forces during wet clean steps, where pattern collapse can readily occur. Care must be taken to reduce surface tension forces during drying and wet cleaning.



Figure 15. Example of resist removal over an array of DRAM storage cells. The DRAM capacitor cells have aspect ratios of > 20:1 causing significant thickness being deposited inside the cells during the masking process. Removal of this resist requires extremely high selectivity to avoid etching or oxidation of the storage cell electrode material, in this case TiN.

7. CONCLUSION

Critical photoresist strip applications are moving away from strong acids and oxidizing plasma chemistries because of concerns for substrate removal or oxidation. Weak Acids, solvents and hydrogen-based plasma chemistries are being explored as solutions to substrate loss issues, but generally have poor residue removal, have lower throughput and can alter junction/dopant characteristics. High mobility channels such as Germanium and II-V materials are intolerant to oxidation, and may require encapsulation to prevent substrate damage during resist removal. Resist strip is no longer a non-interacting process step and must be optimized in conjunction with the process flow to attain acceptable process results.

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