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Roughening of resist-masked Si in buffered HF solutions

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ABSTRACT

HF-based buffered oxide etch (BOE) solutions are commonly used in semiconductor processing for etching SiO_2 selectively to Si in the presence of photoresist masks. This paper reports on an anomalously severe roughening reaction that can occur at Si/resist interfaces when n-type Si is etched in 50:1 BOE solutions (1 wt% HF and 39.5 wt% NH_4F in H_2O) in the presence of certain organic resists. This effect is seen to a very much lesser extent in 9:1 BOE solutions (5 wt% HF and 36 wt% NH_4F in H_2O), and not seen at all in dilute HF solutions (100:1 and 10:1 with 0.5 wt% and 5 wt% HF). The species responsible for the roughening reaction is not identified, but it appears to be related to a breakdown product of the resist. We show that the roughening can be eliminated with the use of a diamond-like-carbon interposer layer under the resist.

INTRODUCTION

Wet etching is widely used in semiconductor processing, and selective etches for SiO_2 (with respect to Si) are among the most widely used and intensively studied. Of these etches, HF-based buffered oxide etch (BOE) solutions are among the most common, with BOE solutions typically viewed as preferable to water-diluted HF (dHF) if there are concerns about the chemical integrity of an organic photoresist mask [1] and/or the adhesion of the resist mask to an oxide underlayer.

This paper focusses on the roughening that can occur at silicon/resist interfaces when silicon is exposed to BOE solutions containing high concentrations of NH_4F. Our experiments were prompted by the anomalously severe roughening observed to occur when n-type Si was exposed to 50:1 BOE solutions (1 wt% HF and 39.5 wt% NH_4F in H_2O) in the presence of certain photoresists. This effect is seen in 9:1 BOE solutions (5 wt% HF and 36 wt% NH_4F in H_2O) to a very much lesser extent, and not seen at all in dHF solutions (100:1 and 10:1 with 0.5 wt% and 5 wt% HF). Si roughening was investigated as a function of silicon resistivity and dopant type, photoresist material, illumination, and etchant (50:1 and 9:1 BOE, and 100:1 and 10:1 dHF). Additional experiments were performed with non-photosensitive organic masking layers, both to help elucidate the mechanisms involved in the roughening reactions and to identify materials that could prevent the roughening if used as an interposer layer under the resist.

EXPERIMENTAL DETAILS

A variety of patterned masking layers, listed in Table I, were fabricated on single crystal, 100-oriented Si wafers having the resistivities and dopant types listed in Table II. Si wafers getting the photoresist-only masks received a hexamethyldisilazane (HMDS) vapor prime at 100 °C and spin-coated with a 450 nm thick layer of Shipley UV110 photoresist ("UV110") or a 825 nm layer of JSR M20G photoresist ("JSR"). The resist was baked on a hot plate at 140 °C prior to exposure (for 60 s) and after exposure (for 90 s). Mask regions to be opened were exposed to 248-nm light in an excimer laser stepper, and development was in a tetramethyl ammonium hydroxide-based developer (Shipley Microposit® LDD - 26W).

Si wafers getting the "resist on (non-photosensitive) interposer" masks got UV110 on a 90 nm thick Shipley AR3 bottom antireflection coating (ARC), or JSR on either a 150 nm thick layer of Shipley LOL-2000 lift-off layer (LOL) or a 100 nm thick layer of diamond-like-carbon (DLC or a-C:H). The ARC (applied without HMDS) was hot plate baked at 140 °C/30 s + 225 °C/60 s prior to resist application. ARC patterning was performed by O_2 reactive ion etching (RIE) using the UV110 resist as a mask. The DLC was deposited by plasma-assisted chemical vapor deposition and patterned by O_2 RIE using the JSR resist as a mask. The LOL (also applied without HMDS) had the same bake treatments as the ARC, and was patterned during the resist develop step with the same developer used to open the JSR resist.

There were four mask types in the "interposer only" group. The ARC-only, LOL-only, and DLC-only masks were prepared from the lithographically patterned ARC/UV110, LOL/JSR, and

DLC/JSR samples described above by selectively removing the resist overlayer with acetone. The poly(methyl methacrylate) (PMMA) masks (approximately 3-5 mm in diameter) were formed from droplets of an 4 wt% solution of PMMA hot plate baked on the samples at 180 ^{o}C for ~30 min.

Etching was performed at room temperature with sample pieces ~2.2 x 2.2 cm^2 in size. Most sample types were evaluated with and without an O_2 RIE descum in case organic residuals remained after the resist develop step. BOE solutions were used as received (Baker Chemical) in concentrations of 50:1 (1 wt% HF and 39.5 wt% NH_4F in H_2O) or 9:1 (5 wt% HF and 36 wt% NH_4F in H_2O). Dilute HF solutions were used as received for the 10:1 concentration (Baker Chemical, 5 wt% HF in H_2O), and diluted in the lab for the 100:1 concentration (0.5 wt% HF in H_2O). After a post-etch rinse in deionized water, the masking layers were typically removed to expose the Si surface topography. Mask removal was accomplished by a combination of an acetone soak (for PMMA and the resist layers) and O_2 ashing for the LOL, ARC, and DLC layers.

Optical micrographs were collected with an Olympus Vanox-T AH-2 microscope equipped with Nomarksi polarizers and a digital camera. Sample topography was sampled by profilometry (Tencor P10). Atomic force microscopy (AFM) was performed on selected samples with a Digital Instruments NanoScope (tapping mode configuration) to evaluate etching-induced roughness not visible optically.

RESULTS AND DISCUSSION

Severe roughening was reproducibly observed to occur in UV110-masked n^+, n, and n^--type Si immersed in 50:1 BOE for 6-10 min. A schematic time progression of this etching is shown in Figs. 1a - 1d, where Fig. 1a shows a Si sample before any etching, with the resist still in place, and Figs. 1b - 1d show samples after etching and resist removal. Optical micrographs corresponding to Figs. 1c and 1d are shown in Figs. 2a (6.1 min) and 2b (10 min) for n^--type Si. A very rough, irregularly featured Si surface is left at the edges of regions originally covered with resist, a topography that contrasts with the very smooth Si surfaces where the resist was open. Si trenches at the resist edges were typically 50 nm deep after 6.1 min and about 80-300 nm deep after 10 min in 50:1 BOE, with the deepest "trenching" typically found around small (~10 µm) isolated features with a large perimeter to area ratio. This deep trenching topography was similar in magnitude for n^+, n, and n^--type Si samples, weaker but detectable in p^--type Si samples, and completely absent in p-type or p^+-type Si samples.

The degree of roughening was insensitive to sample illumination; for a given type of Si, there was no apparent difference between samples etched for 10 min under normal laboratory lighting and those etched in the dark. The degree of roughening in these UV110-masked samples was similarly insensitive to whether or not the samples received a descum sufficent to remove 30 nm of the resist.

The severity of the roughening was dependent on the type of HF solution. No signs of roughening were seen for any type of UV110-masked Si immersed in 10:1 or 100:1 dHF for 10 min. Optical microscopy of n^- and p^-- type Si samples exposed to 10 min of 9:1 BOE showed a clear transfer of the mask pattern (resulting from Si removal from the open regions of the mask) as well as

faint hints of roughening at the edges of regions of the Si originally covered by resist. Fig. 3 shows these features for the n^--type Si sample. Etch steps (measured by profilometry) were ~12 and 8 nm deep for n^- and p^--type Si respectively; etch steps in p^+-type Si samples were barely visible by optical microscopy and not locatable in the profilometer microscope. It thus appears that both roughening and etching are faster in n-type Si than p-type Si. This is not particularly remarkable, in that a variety of wet etch chemistries exhibit dopant-dependent Si etch rates [2], a fact often exploited in designing etch stop layers [3, 4].

The different roughening behaviors seen in these different HF solutions suggest that the roughening may be more affected by solution pH (or other aspects of the solution chemistry) than by the HF concentration. In line with these results, Si roughening (on a very much milder scale than observed here) was also found to be worse with BOE than with dHF. In this case [5], the average surface roughness of bare n^--type 100 Si wafers was found to be ~0.6 nm after a 10 min clean in BOE but ~0.4 nm after a 10 min clean in dHF. Similar findings were also reported in Ref. 6.

The fact that the Si roughening is worst just inside the resist edges suggests that the etching/roughening reaction is fastest in regions where the resist and Si are in close proximity. The delayed onset of the roughening further suggests that a breakdown product of the resist may play a key role in the reaction. In an attempt to elucidate the mechanisms involved in this roughening reaction and to identify mask materials that might minimize the roughening, we proceeded to examine how the roughening of n^--type Si induced by a 10 min 50:1 BOE etch depended on the type of masking layer. The results are summarized in Table I.

We first changed the resist type from UV110 to JSR. Non-descummed JSR samples showed topographies ranging from the typical mild roughening shown in Fig. 4 to roughening comparable to that shown in Fig. 2b for UV110. However descummed JSR samples (with O_2 RIE descum treatments to remove 30 - 100 nm of the 800 nm post-develop JSR thickness) all showed severe roughening similar in degree and character to that seen with UV110. While it is possible that the descum was producing a plasma modification of the resist, the similarity of the results for the (non-descummed) UV110 and descummed JSR suggests that the primary effect of the descum is to clear organic residuals from the open regions of the mask, thus ensuring unobstructed exposure of the Si to the etchant.

ARC/UV110 and ARC-alone samples also showed severe roughening (as bad or worse than that seen with UV110), and some trenching was seen at the edges of PMMA droplet masks.

Fig. 5 shows the topography typically seen with LOL-alone and descummed LOL/JSR samples etched for 10 min in 50:1 BOE. The samples had smooth Si in the resist openings, and an overlapping array of "edge bubble" features in the borders around the mask openings. The edge bubbles were typically about 5 μm in diameter and about 20 - 30 nm deep. It thus appears that edge roughening in 50:1 BOE can be substantially reduced (though not completely eliminated) by using LOL or LOL/JSR instead of JSR (or UV110) alone.

The non-descummed LOL/JSR sample showed a mix of two distinct topographies: a sparser version of the edge bubble topography seen for the LOL-alone and descummed LOL/JSR samples, and a uniform, fine-grained roughening of the Si in the areas of the resist openings. Again, we attribute this mixed topography to the protective effect of residual organics in present in some of the resist openings. The similarity of the roughening in the non-descummed LOL and descummed LOL/JSR samples suggests that the acetone rinse used to remove the JSR from the LOL may also function as a descum.

In contrast to the results for the polymeric organic masks deposited from solution, *no* Si roughening or trenching was seen in samples masked with DLC-alone or DLC/JSR. This is shown in the AFM of Fig. 6 for the case of the DLC mask. Since DLC is a chemically inert material that is resistant to organic solvents as well as most known acids and bases [7], this finding further supports the idea that a breakdown product of the resist is needed for the edge roughening. This hypothetical resist breakdown product could be produced directly (in "resist + BOE" reactions) or indirectly (from reactions of the resist with a "Si + BOE" etch product).

The chemical complexity of these concentrated BOE solutions [8-10] prevents us from unequivocally identifying the component of the BOE solution likeliest to be responsible for the roughening reaction. In addition to HF monomers, secondary species such as HF_2^- and the dimer $(HF)_2$ are also present in significant amounts, depending on solution pH and fluoride concentration $[F^-]$. In our BOE solutions, with $[F^-] \simeq 11$ M (from NH_4F) and pH values calculated to be in the range 3.8-4.5 [11], the dominant species should be HF_2^- [8, 9]. In contrast, our dHF solutions have pH values in the range 1-2 [11] and no NH_4F; the dominant species in these solutions should be HF or $(HF)_2$ [9]. It thus seems possible that HF_2^- is the component of the BOE solution most involved with the photoresist breakdown and Si roughening, a scenario made more plausible by studies of oxide etching in BOE [8] showing that HF_2^- etches SiO_2 five times faster than HF.

CONCLUSIONS

It was found that 50:1 BOE solutions can produce an anomalously severe roughening in n-type Si in the presence of certain resists. This effect is seen to a very much lesser extent in 9:1 BOE solutions, and not seen at all in 100:1 and 10:1 dHF solutions. The species responsible for the roughening was not identified, but it appears to be related to a breakdown product of the resist. It was shown that the roughening can be reduced with the use of a LOL layer under the resist and eliminated with the use of a diamond-like-carbon interposer layer under the resist.

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11. pH in the BOE solutions was calculated using $[H^+]= k[HF]/[F^-]$ with $k = 6.3 \times 10^{-4}$ M, $[F^-] \simeq 11$ M (from NH_4F), and [HF] = 0.6 M (for 50:1 BOE) or 2.8 M (for 9:1 BOE). pH in the dHF solutions was calculated using $[H^+] = (k[HF])^{0.5}$ with [HF] = 0.29 M (for 100:1 dHF) or 2.6 M (for 10:1 dHF).

FIGURE CAPTIONS

1. Schematic time progression of roughening in UV110-masked n^--type Si in 50:1 BOE, shown in cross-section: "0 min" (a); "2.5 min" (b); "6.1 min" (c); "10.0 min" (d). The horizontal dotted lines indicate the original position of the Si surface, and the vertical dashed lines indicate the original position of the resist (which was removed after etching for b-d). The vertical scale is qualitative only.

2. Optical micrographs of a UV110-masked n^--type Si surface after 6 min (a) or 10 min (b) in 50:1 BOE. The square and lines were open regions in the resist, which was stripped by acetone after the BOE etch.
3. Optical micrographs of a UV110-masked n^--type Si surface after 10 min in 9:1 BOE. The square and lines were open regions in the resist, which was stripped by acetone after the BOE etch.
4. Optical micrograph of a JSR-masked n^--type Si surface after 10 min in 50:1 BOE. The selected area is shows an example of the fairly typical "mild" edge roughening. The squares were open regions in the resist, which was stripped by acetone after the BOE etch.
5. Optical micrograph of a LOL/JSR-masked n^--type Si surface exposed to 10 min of 50:1 BOE after an O_2 descum sufficient to remove 100 nm of resist the 800 nm resist. The squares were open regions in the mask, which was stripped after the BOE etch by a combination of acetone (for the JSR) and O_2 ashing (for the LOL).
6. AFM of a DLC-masked n^--type Si surface exposed to 10 min of 50:1 BOE. The resist was stripped by acetone before the BOE etch, and the DLC was removed by O_2 RIE after the BOE etch. Dark regions in the image indicate a uniform etch step of 7 nm in the open regions of the mask.

Table I. Summary of tested sample geometries and masking materials along with a description of the roughening produced on n^--type Si after 10 min in 50:1 BOE. Mask processing details are indicated in the HMDS and O_2 RIE columns.

Geometry	System	Materials	HMDS	O_2 RIE	Roughening on n^--type Si
	Single photosensitive layer ("resist only")	UV110 (450 nm)	Under UV110	No	Severe (Fig. 2b)
		JSR (825 nm)	Under JSR	No	Mixture ranging from mild (Fig. 4) to severe
		JSR (825 nm) + 6 or 30 s descum	Under JSR	Yes	Severe
	Single non-photosensitive layer ("interposer alone")	ARC (90 nm)	None	Yes	Severe
		LOL (150 nm)	None	No	Dense edge bubbles
		PMMA	None	No	Edge trenching
		DLC (100 nm)	None	Yes	None
	Photosensitive resist on interposer	ARC/UV110	None	Yes	Severe
		LOL/JSR	None	No	Mixture of sparse edge bubbles and uniform open-area roughness (Fig. 6)
		LOL/JSR + 30 s descum	None	Yes	Dense edge bubbles (Fig. 5)
		DLC/JSR	Under JSR	Yes	None (Fig. 7)

Table II. Description of Si wafer types and resistivities.

Si type	Dopant	ρ, Ω-cm
n^-	P	11-25
n	P	0.6-1.5
n^+	Sb	0.0008-0.01
p^-	B	11-25
p	B	1-2
p^+	B	0.008-0.01

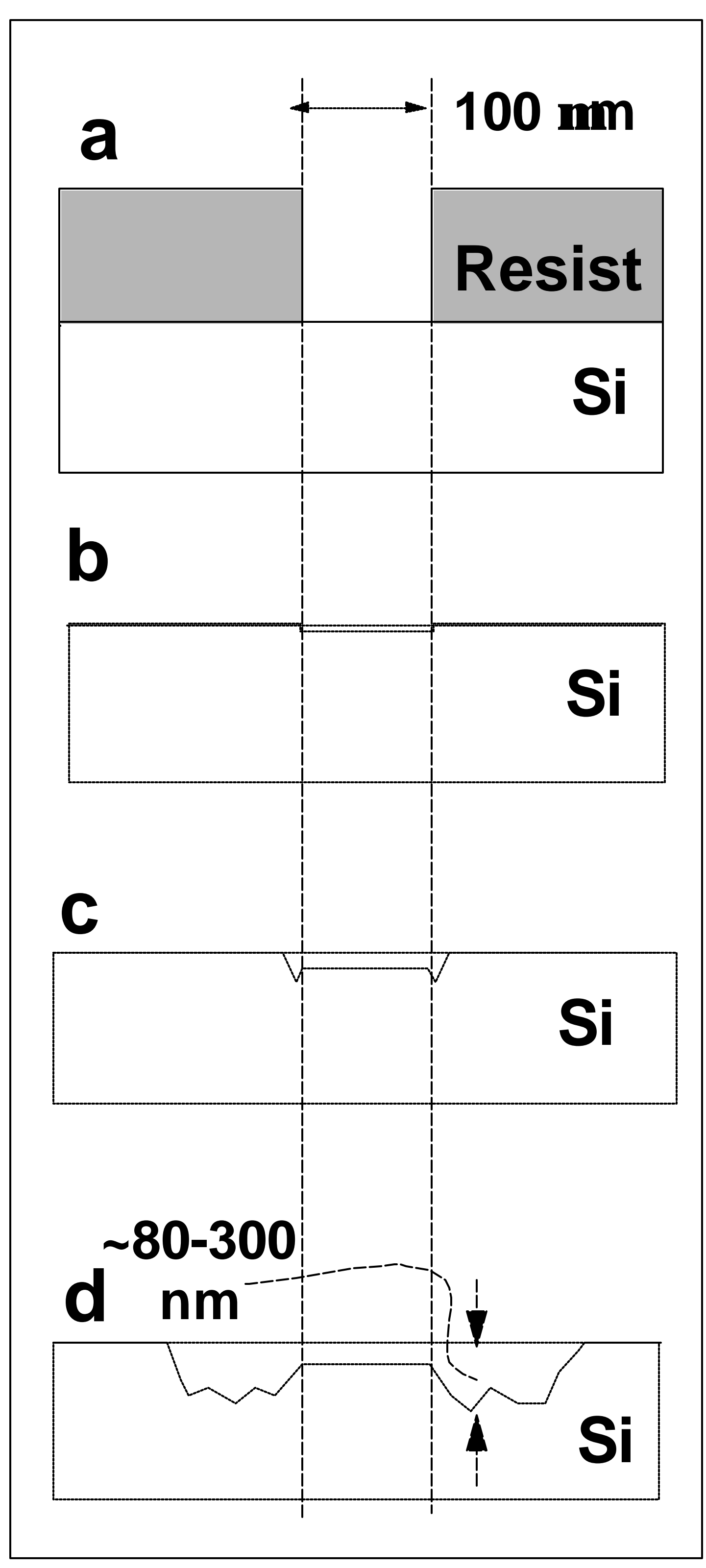

Fig. 1. Schematic time progression of roughening in UV110-masked n^--type Si in 50:1 BOE, shown in cross-section: "0 min" (a); "2.5 min" (b); "6.1 min" (c); "10.0 min" (d). The horizontal dotted lines indicate the original position of the Si surface, and the vertical dashed lines indicate the original position of the resist (which was removed after etching for b-d). The vertical scale is qualitative only.

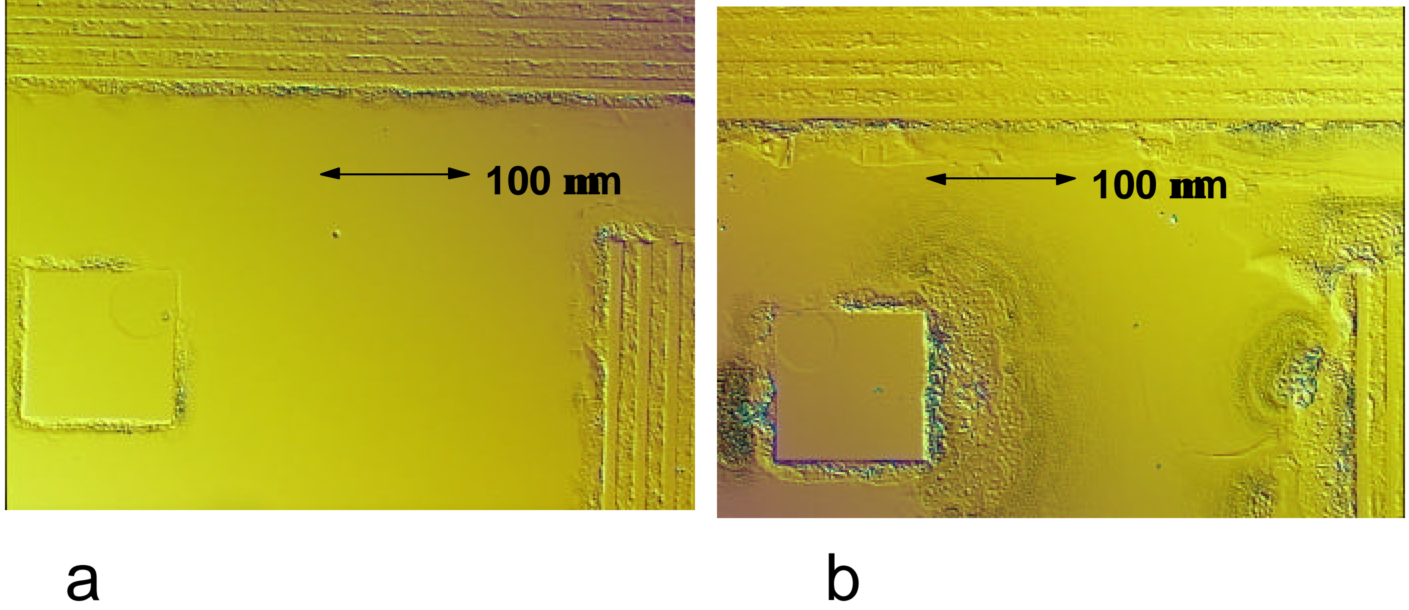

Fig. 2.Optical micrographs of a UV110-masked n^--type Si surface after 6 min (a) or 10 min (b) in 50:1 BOE. The square and lines were open regions in the resist, which was stripped by acetone after the BOE etch.

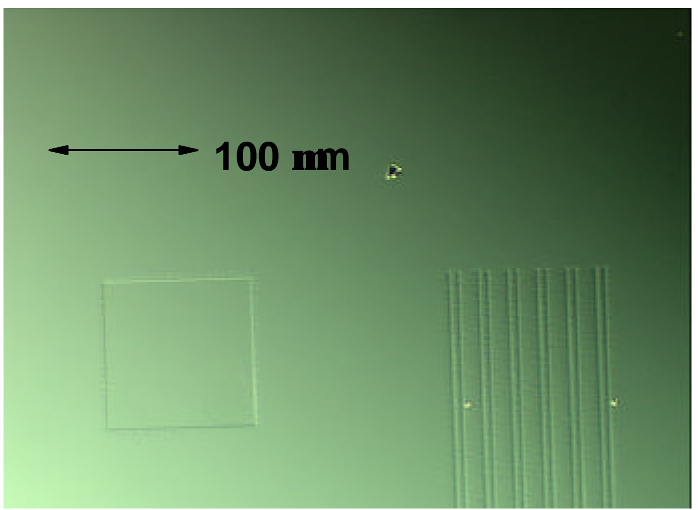

Fig. 3. Optical micrographs of a UV110-masked n^--type Si surface after 10 min in 9:1 BOE. The square and lines were open regions in the resist, which was stripped by acetone after the BOE etch.

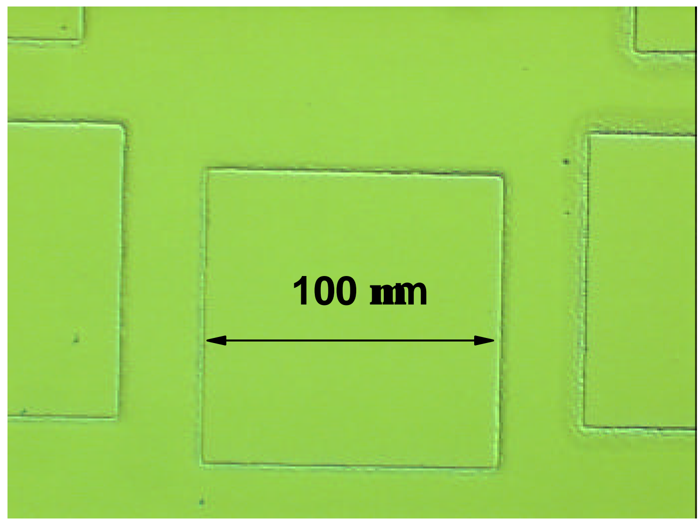

Fig. 4. Optical micrograph of a JSR-masked n$^-$-type Si surface after 10 min in 50:1 BOE. The selected area is shows an example of the fairly typical "mild" edge roughening. The squares were open regions in the resist, which was stripped by acetone after the BOE etch.

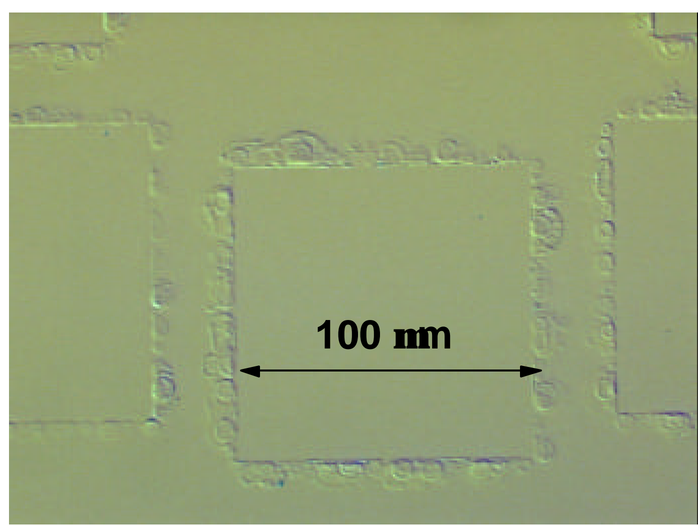

Fig. 5. Optical micrograph of a LOL/JSR-masked n--type Si surface exposed to 10 min of 50:1 BOE after an O2 descum sufficient to remove 100 nm of resist the 800 nm resist. The squares were open regions in the mask, which was stripped after the BOE etch by a combination of acetone (for the JSR) and O2 ashing (for the LOL).

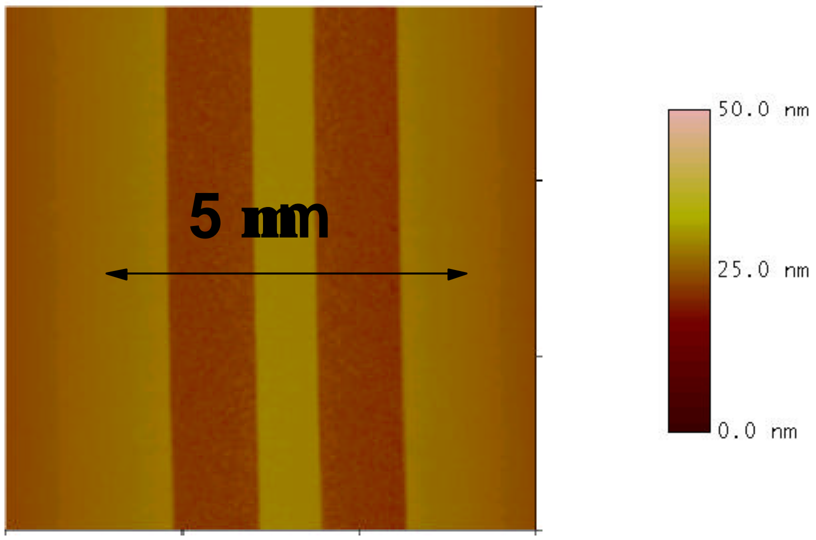

Fig. 6. AFM of a DLC-masked n^--type Si surface exposed to 10 min of 50:1 BOE. The resist was stripped by acetone before the BOE etch, and the DLC was removed by O_2 RIE after the BOE etch. Dark regions in the image indicate a uniform etch step of 7 nm in the open regions of the mask.