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Katherine L. Saenger, Steven E. Steen, Steven J. Koester
IBM Research Division
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

Research Division
Almaden - Austin - Beijing - Delhi - Haifa - India - T. J. Watson - Tokyo - Zurich

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Anomalous etching of n-type Si in buffered HF solutions

Katherine L. Saenger, Steven E. Steen, and Steven J. Koester
IBM Research
T.J. Watson Research Center
Yorktown Heights, NY 10598

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. In contrast to the nearly undetectable rates of Si etching in dilute HF (dHF), BOE solutions were found to etch n-type Si at $\gtrsim$1 nm/min. In addition, an anomalously fast and catastrophic etching mode was seen for n-type Si in 50:1 BOE solutions (1 wt% HF and 39.5 wt% NH_4F in H_2O) in the presence of certain photoresists, an effect not seen in 9:1 BOE solutions (5 wt% HF and 36 wt% NH_4F in H_2O) or in dHF (100:1 and 10:1 with 0.5 wt% and 5 wt% HF). It is suggested that alternatives to BOE may be preferred for oxide etches requiring a hard stop on n-type Si, and that the etching of n-type Si in BOE can be accelerated by resist degradation products.

INTRODUCTION

High performance integrated circuits are often fabricated in specially tailored surface layers (such as silicon-on-insulator and strained silicon) whose vertical dimensions must be carefully controlled in order preserve the targeted device characteristics [1]. It is therefore important to understand how the various processing steps of device fabrication may contribute to unintended surface layer thinning.

This paper focuses on the unexpectedly high etch rates observed for n-type single crystal Si in HF-based buffered oxide etch (BOE) solutions containing high concentrations of NH_4F. HF-based solutions are widely used for etching SiO_2 selectively with respect to Si, with BOE solutions typically being preferred over water-diluted HF (dHF) in cases where an organic photoresist mask needs to be preserved [2]. However, in contrast to the nearly undetectable rates of Si etching in dHF, BOE solutions were found to etch n-type Si at an etch rate of ~1 nm/min. In addition, we find that BOE solutions can support an anomalously fast (and catastrophic) Si etching mode in the presence of certain photoresists, an effect that is not seen in dHF etches with the same HF concentration.

Si etching through an organic mask was investigated as a function of silicon resistivity and dopant type (n or p), resist material, and etchant (50:1 and 9:1 BOE, and 100:1 and 10:1 dHF). The etching was investigated in two time regimes: short times (where it was assumed that the resist mask did not contribute to the etching) and long times (where resist degradation appeared to contribute to a catastrophic etching mode). Additional experiments were performed with different combinations of masking layers to help elucidate the mechanism for the catastrophic etching.

EXPERIMENTAL DETAILS

Single crystal, 100-oriented Si wafers with different resistivities and dopant types (n or p) were prepared with a variety of patterned masking layers. Si wafers in a first group were given a hexamethyldisilazane (HMDS) vapor prime at 100 ºC and spin-coated with a 4500 Å thick layer of Shipley UV110 photoresist which was patterned by a 248-nm excimer laser stepper. The resist was baked on a hot plate at 140 ºC prior to exposure (for 60 s) and after exposure (for 90 s). The resist was typically removed (by acetone) after the wet etch to make it easier to inspect the Si surface.

Si wafers in a second group were also patterned lithographically, but with different combinations of resists (JSR M20G or Shipley UV110) and bottom anti-reflection coatings (ARCs, Shipley AR3). The JSR had a thickness of 8250 Å, and the same HMDS prime and bake treatments as the UV110. The 900 Å ARC was hot plate baked at 140 ºC/30 s + 225 ºC/60 s prior to resist application. ARC patterning was performed by O_2 reactive ion etching (RIE) through a photoresist mask. Photoresist on the ARC-only samples was removed by acetone. Other wafers in this second group received a 150-260 Å thick layer of "low-temperature oxide" (LTO) SiO_2 (deposited with a low-temperature chemical vapor deposition process) prior to lithographic patterning.

Wafer pieces in a third group were masked by materials that were not lithographically patterned. Some samples were masked with pipette-dispensed droplets of poly(methyl methacrylate) (PMMA) solution (4 wt% PMMA in anisole) baked in air at 180 ^{o}C for ~30 min. Others were masked with a 1800 Å-thick layer of amorphous diamond-like-carbon (DLC or a-C:H) deposited by plasma-assisted chemical vapor deposition and patterned by an O_2 RIE process using a metal contact mask.

Wafers were cut into pieces ~2.5 x 2.5 cm^2 in size and etched with room temperature solutions in beakers. 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). Samples were rinsed in deionized water after the desired etch time, and then soaked in acetone to remove the resist. If necessary, the remaining ARC was removed with a second O_2 RIE.

Optical micrographs were collected with an Olympus Vanox-T AH-2 microscope equipped with Nomarksi polarizers and a digital camera. Etch steps above 30 Å in height were easily measured by profilometry (Tencor P10) and clearly visible by Nomarski. Step heights much smaller than 30 Å could be seen with Nomarski, but could not be profiled because they lacked enough contrast to be located in the P10 microscope. Etch rates for samples with steps below the P10 detection limit are thus given as an upper limit, based on the upper limit step height of 30 Å.

RESULTS AND DISCUSSION

Table I lists the etch rates of 100-oriented single crystal silicon as a function of dopant type and etch solution. Etch times were kept short enough to prevent complications of masking layer erosion and delamination. Etching in 10:1 HF was extremely slow (<3 Å/min) for all Si-types. In contrast, Si etch rates in 50:1 and 9:1 BOE were relatively high (9-12 Å/min) for n^-, n, and n^+-type Si, measurable for p^--type Si (~5-8 Å/min), and barely detectable for p and p^+-type Si.

Dopant-dependent etch rates are not uncommon. They have been reported for a variety of Si wet etch chemistries [3] and are often exploited in designing etch stop layers [4, 5].

A distinctly different, anomalous type of etching was reproducibly observed to occur in n^+, n, and n^--type Si immersed in 50:1 BOE for longer etch times (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 a UV110-masked n^--type Si. The anomalous etching leaves a very rough, irregularly featured Si surface at the edges of regions originally covered with resist, a morphology that contrasts with the very smooth Si surfaces where the resist was open. Si trenches at the resist edges were typically 500 Å deep after 6.1 min and about 1500-3000 Å 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 absent in p-type or p^+-type Si samples.

This anomalous etching was not seen in UV110-masked Si after 10 min in 100:1 dHF, 10:1 dHF, or 9:1 BOE. For the case of 9:1 BOE, clean etch steps are clearly visible in n^- and p^--type Si samples, and barely visible in p^+-type Si samples, consistent with the etch rate data of Table I. The n^--type and p^--type Si samples also showed faint hints of roughening in regions originally covered by resist, as can be seen in Fig. 3 for the case of the n^--type sample. No signs of roughening were seen for any of the 10:1 dHF samples.

While the absence of the anomalous etching effect in the dHF samples might possibly be a consequence of the extremely low etch rates of Si in dHF, this explanation does not account for differences between 50:1 and 9:1 BOE, which have similar Si etch rates. One might, in fact, even expect the anomalous etching to be worse in the 9:1 BOE than 50:1 BOE, since 9:1 BOE has the higher HF concentration (5 wt% vs. 0.5 wt%). However, the chemistry of BOE solutions is known to be quite complicated [6]. Component species HF and HF_2^- have very different etch characteristics (HF_2^- reportedly etches oxide 5x faster than HF), and the relative amounts of HF and HF_2^- can be strongly affected by solution pH (HF_2^- is expected to be more of a dominant etch species in higher pH BOE solutions) [7]. The 9:1 BOE solution has a lower pH: ~3.5 vs. ~4.2 for 50:1 BOE (based on $[H^+] = k*[HF]/[F^-]$, with $k = 1.3 \times 10^{-3}$ M and [HF] and $[F^-]$ taken from the initial concentrations of HF and NH_4F).

The location of the anomalous etching under the resist edges suggests that some component of the resist plays a role in the etching. The delayed onset of the anomalous etching further suggests that the key component may be a breakdown product of the resist. Etch experiments with 50:1 BOE were performed with a variety of masking layers to help elucidate the etch mechanism.

We first examined the effect of resist type on n^--type Si samples given 10 min etches. Anomalous etching very similar to that seen with UV110 alone was also seen with lithographically patterned masks of ARC/UV110 and ARC alone. Anomalous etching was also present in n^--Si samples with lithographically patterned JSR, but it was less severe and limited to a 5-10 μm border around the resist openings. Anomalous etching/trenching was also seen at the edges of PMMA droplet masks (exposed to the etchant both under normal illumination and in the dark). However, *no* anomalous Si etching was seen when the mask was a patterned layer of DLC. Because DLC is highly chemically inert (it is resistant to organic solvents as well as most known acids and bases [8]), this finding further supports the idea that a breakdown product of the resist contributes to the anomalous etching.

We next examined etching through patterned photoresist masks on n^--type Si/SiO_2 samples to see if the anomalous etching would still occur when the Si and the resist were not in direct contact. Unfortunately, the samples did not provide a completely clean experiment because oxide etch-back (often accompanied by resist delamination) introduced new opportunities for resist/Si contact. However, a comparison of the Si surfaces in Fig. 4a (n^--type Si masked with

SiO_2 and UV110, etched in 50:1 BOE for 9 min, including 1 min to open the SiO_2) and Fig. 4b (n^--type Si masked with UV110 only, etched in 50:1 for 8 min) show several significant differences. In samples without SiO_2, the Si in the resist openings remained smooth, and the rough trenching extended many tens of microns away from the resist opening. In contrast, trenching in samples with SiO_2 was localized to a narrow ~5 µm region at the resist edges, and the Si in the resist openings was often rough. Differences in morphology are highlighted in Figs. 4c - 4e, which show regions near the edges of the 100 µm squares at high magnification. Figs. 4c - 4d show rough and smooth squares from the sample of Fig. 4a (with SiO_2), and Fig. 4e shows the highly textured edge region of a square from the sample of Fig. 4b (without SiO_2). Overall, these oxide sample results can best be explained with a solution-mediated etch mechanism requiring only resist/Si proximity, not contact. SiO_2 left intact under the resist in these samples protects the underlying Si from the widespread trenching, but leaves a higher concentration of unconsumed reactive species available to attack exposed Si in the resist openings.

These results make it clear that the anomalous Si etching in 50:1 BOE requires the presence of both a susceptible resist and exposed areas of "etchable" n-type Si. Interestingly, Figs. 5a - 5b suggest that the degradation behavior of UV110 in 50:1 BOE may depend on the substrate type. Resist on p^+-type (Fig. 5a) and unpatterned ARC (not shown) exhibit a profusion of small bumps (50 nm high, 5 µm diam) after immersion times of 8 min. In contrast, resist on n^--type Si (Fig. 5b) is disrupted in regions near the anomalous etching, but is largely free of the bumps.

None of this data is sufficient to definitively identify the particular species responsible for the etching. The species could be produced by a "resist + BOE" reaction (and etch n-type Si much faster than p-type Si), or it could be the product of a "resist + Si etch product" reaction (and be more damaging to n-type Si simply because the faster-etching n-type Si produces more of the hypothetical Si etch product intermediate). Alternatively, the etching mechanism could be something more complicated, perhaps, for example, a Si etch product such as SiF_6^{-2} reacting with H_2O near the Si surface to produce OH^- (a known antagonist to resist) in surface-localized regions of high pH.

CONCLUSIONS

BOE solutions (50:1 and 9:1) were found to etch n-type Si at $\gtrsim$1 nm/min, a fact that should be kept in mind when planning the wet etch and clean steps to which the device-critical surface Si layers will be exposed. In addition, it was found that 50:1 BOE solutions comprising 5 wt% HF and 39.5 wt% NH_4F produced an anomalously fast (and catastrophic) etching mode in n-type Si in the presence of certain resists, an effect that was not seen in 9:1 BOE solutions (5 wt% HF and 36 wt% NH_4F in H_2O) or in dHF (100:1 and 10:1 with 0.5 wt% and 5 wt% HF). The species responsible for the anomalous etching was not identified, but it appears to be related to a breakdown product of the resist. These results suggest that alternatives to BOE may be preferred for oxide etches requiring a hard stop on n-type Si, and that the etching of n-type Si in BOE can be accelerated by resist degradation products.

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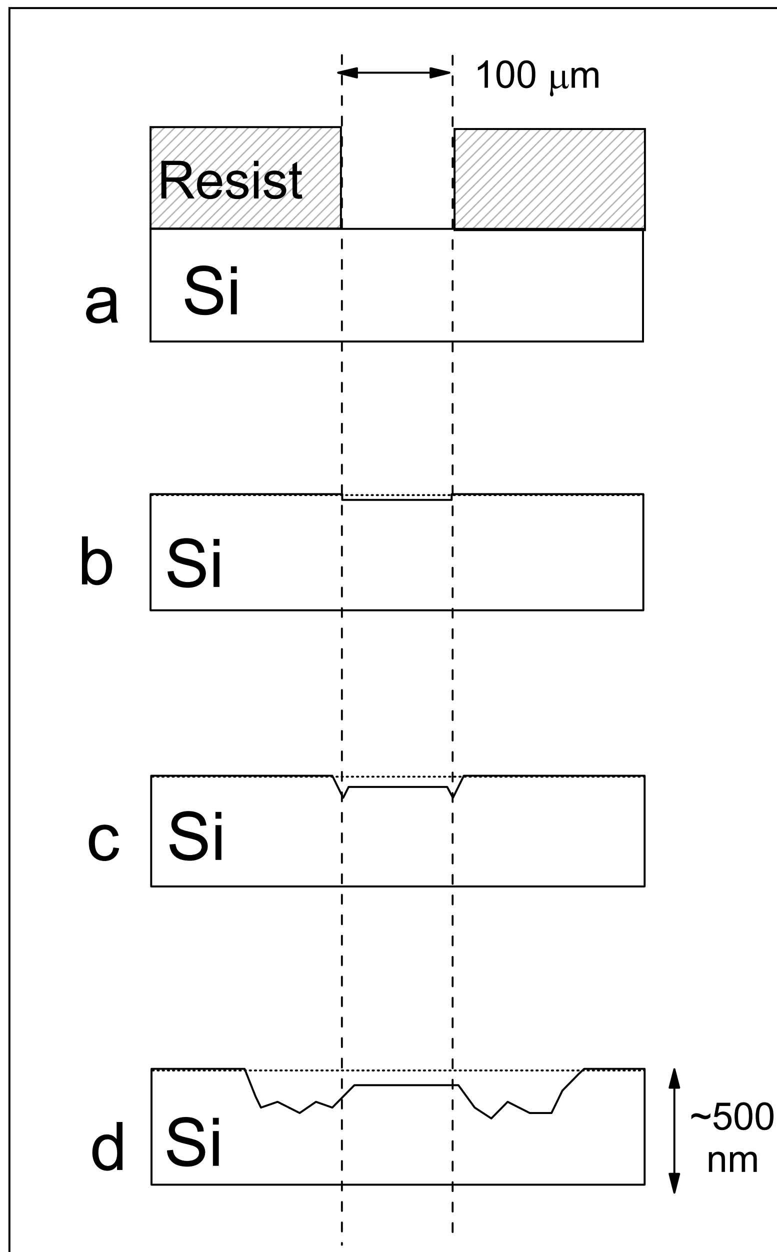
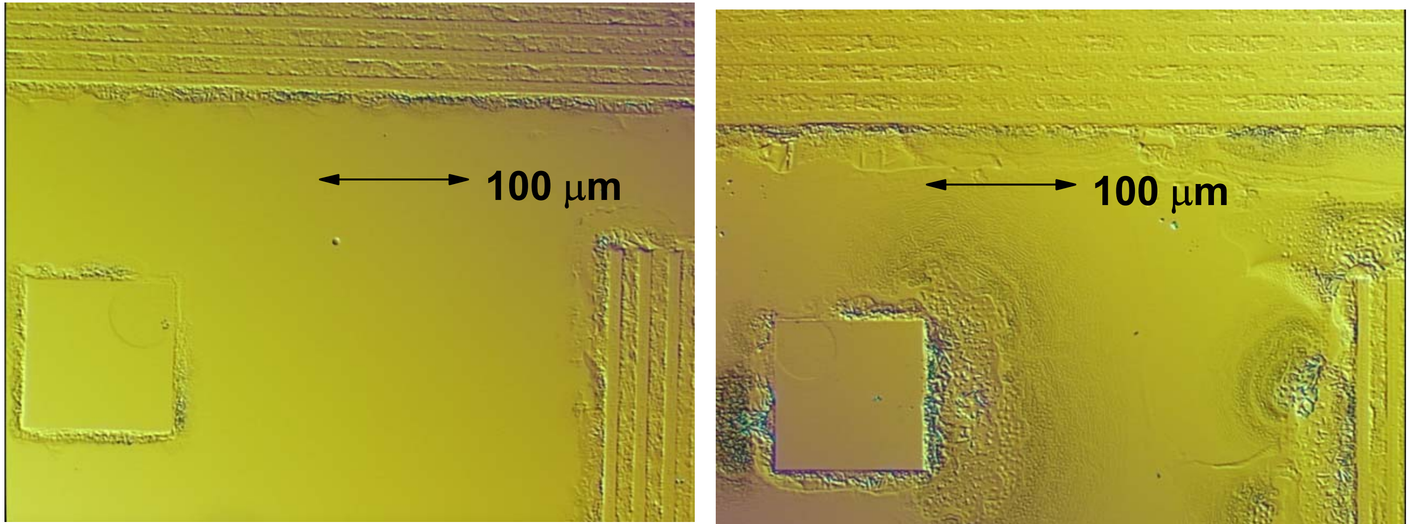


Fig. 1. Schematic time progression of anomalous Si etching in 50:1 BOE, shown in cross-section: "0 min" (a); "2.5 min" (b); "6.1 min" (c); "10.0 min" (d). The horizontal dotted lines indicate the original position of the Si surface, and the vertical dashed lines indicate the original position of the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



a b

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

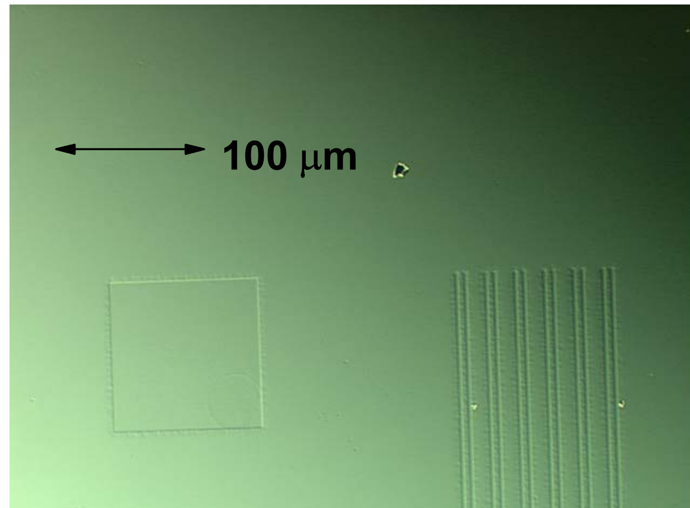
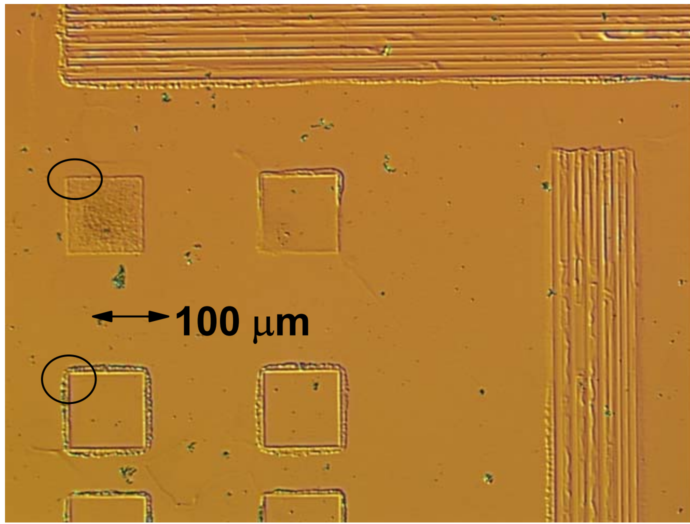
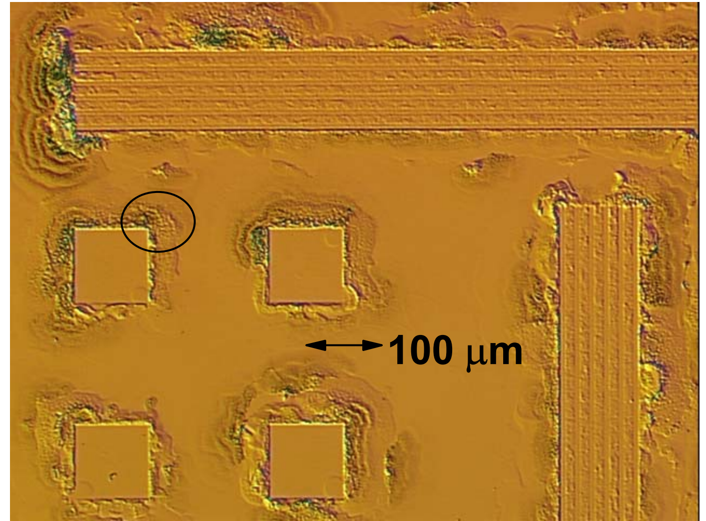


Fig. 3. Optical micrographs of Si surfaces showing the etch steps produced in n^--type Si by 10 min in 9:1 BOE. As before, the square and lines were open regions in patterned UV110 resist, which was stripped by acetone after the BOE etch.



a



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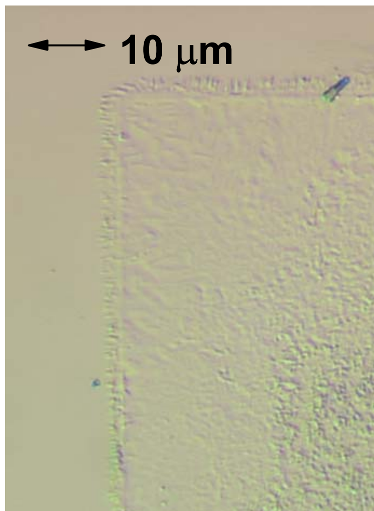

c

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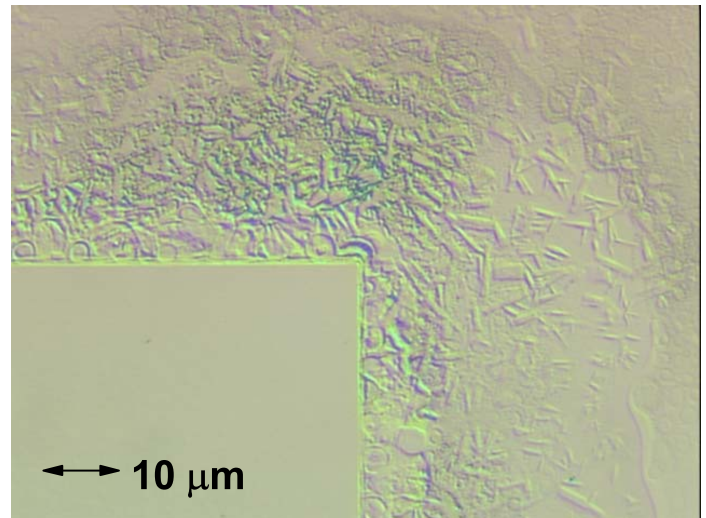
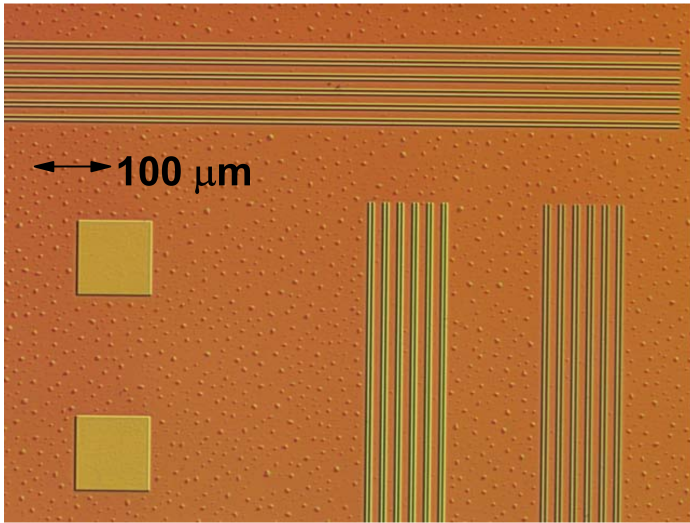
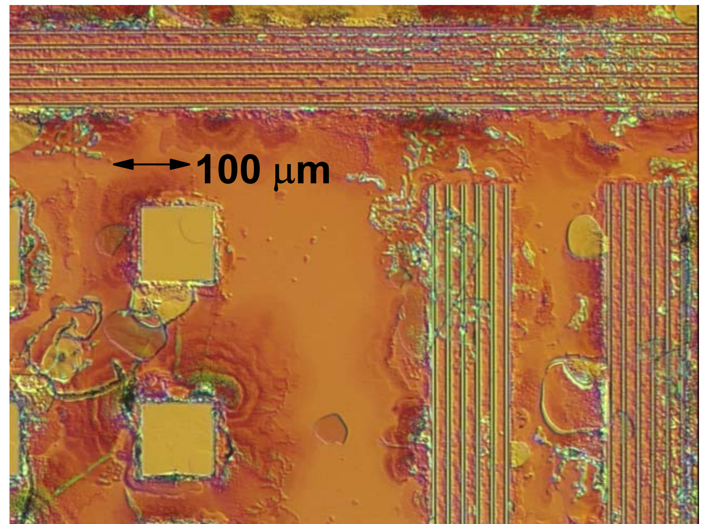


e

Fig. 4. Optical micrographs of n^--type Si etched in 50:1 BOE, with and without a LTO layer between the resist and Si substrate. Low magnification: with LTO (a); without LTO (b). High magnification: with LTO, a rough square (c); with LTO, a smooth square (d); without LTO, the rough Si outside a square (e). Etch times were 8 min for bare Si and 9 min for the LTO samples. As before, the squares were open regions in patterned UV110 resist, which was stripped by acetone after the BOE etch.





a

b

Fig. 5. Optical micrographs of patterned UV110 after 8 min in 50:1 BOE, as a function of material under the resist: p+-type Si (a); n⁻-type Si (b).

Table I. Etch rates of 100-oriented single crystal silicon as a function of dopant type and etch solution. UV110 was used as a mask. Uncertainties are roughly ±20%, due to variations in step measurements.

			10:1 dHF		50:1 BOE		9:1 BOE	
Si-type	Dopant	ρ, Ω-cm	Etch rate, Å/min	Etch time, min	Etch rate, Å/min	Etch time, min	Etch rate, Å/min	Etch time, min
n^-	P	11-25	<<3	10.1	11	4.0	12	6.1
n	P	0.6-1.5	<<3	10.1	9	4.0	11	6.1
n^+	Sb	0.008-0.01	<<3	10.1	9	4.0	12	6.1
p^-	B	11-25	<<3	10.1	5	8.0	8	6.1
p	B	1-2	-	-	<<3	10.0	-	-
p^+	B	0.008-0.01	<<3	10.1	<<3	8.0	<<3	6.1