Spontaneously forming 30-150Å Defects at the Si/oxide interface

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Introduction

Silicon wafers, which have been exposed to air after being prepared by ion milling, show defects on the surface in size of the order of 30-150Å. Comparing this with the diameter of argon bubbles, which is reported to be 180-350Å [1] leads to the presumption that the origin of these defects is a different one.

Looking at a specimen that was prepared several months ago, defects were found. After a brief look, the specimen was left in the transmission electron microscope, which was turned off, for several hours. Afterwards the amount of defects had increased. This further supported the idea that the defects are not a direct product of the ion milling process.

Experimental

A previously perforated planar TEM specimen of silicon sample (8GLJH-060) was ion milled for 10s using two argon guns at an angle of 20°, 0.5mA per gun and a fixed voltage of 4kV. The time the specimen surface was in contact with air was minimized to 3min, by taking it out of the ion mill and putting it in the electron microscope airlock immediately afterwards. The silicon wafer was left in the vacuum of the microscope for ~14 hours and afterwards exposed to air for two hours, with another two hours pumping down afterwards.

Another preparation of the sample was to dip it for 1s in a dilution of HNO_3, HF and water at a ratio of 3:1:3. To stop the acid reaction it was then dipped in water and methanol, and then (as above) rapidly placed into the electron microscope.

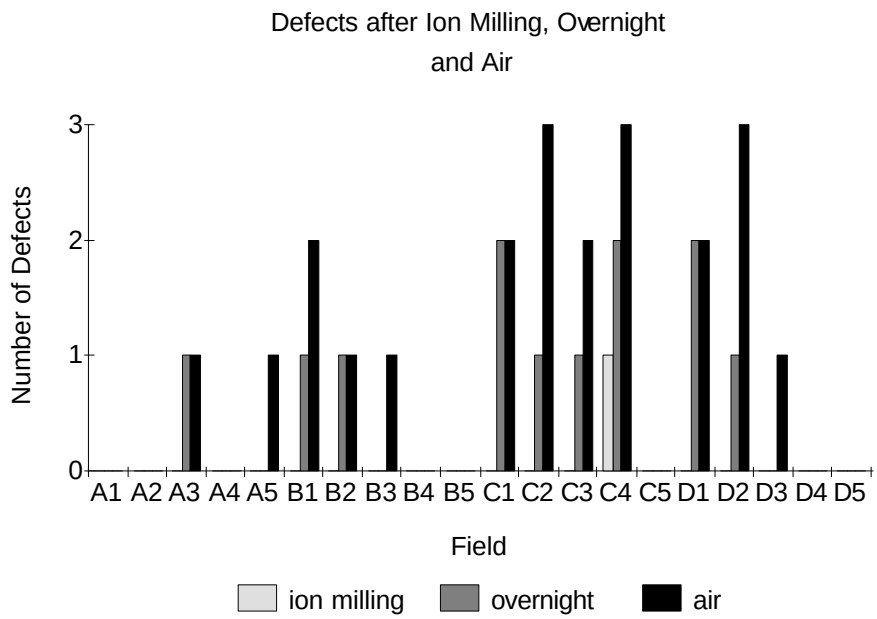
To measure the density of the defects versus time, a new specimen (87GEPO-025) was ion milled, under the same conditions as above and left in the microscope for 26.5 hours. For the first 13 hours the density was measured every two hours with a delay of one hour, which was needed to pump the system down. After this treatment, the silicon wafer was exposed to air for two hours in order to find out if this increased the density.

Results and Discussion

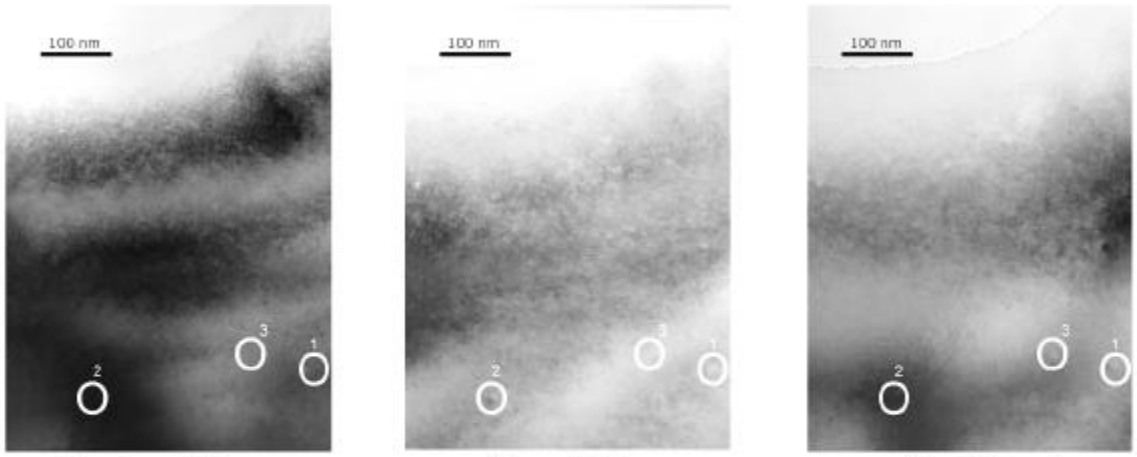
Cumulative counts of defects of size 30-150Å in different regions show that the density varies, but the growing rate is nearly the same (Table 1). The thickness in the considered regions was approximately the same. This and the fact that they can be removed by very short periods of ion milling, leads to the conclusion that the defects are on the surface and

not in the bulk. Further Table 1 and Fig. 1 demonstrates that different ways of storage cannot suppress the growth of the defects. But the growing rate in air is at least four-times as high as in the vacuum of ~50mTorr in the microscope.

Treatment	Ion milled	In microscope for ~14h	In air for 2h
Density (region I)	$3.1*10^8$ 1/cm^2	$23*10^8$ 1/cm^2	$34*10^8$ 1/cm^2
Density (region II)	$1.7*10^8$ 1/cm^2	$17*10^8$ 1/cm^2	$22*10^8$ 1/cm^2



Comparing images of these stages in the same location shows that existing defects stay and new ones are forming, as shown in picture 1.



after ion milling | after ~14h in microscope | after 2h in air

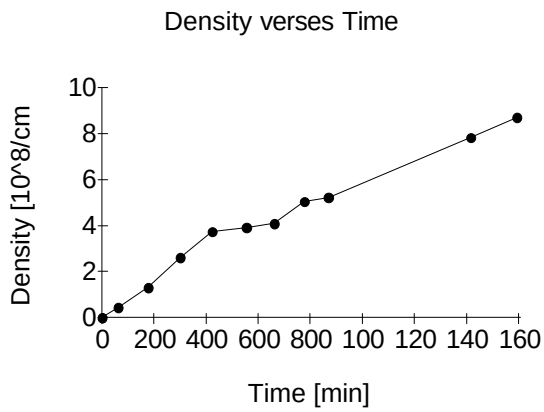
Three eventual defect locations, numbered 1 through 3, changed with time as follows:
1 being there at the beginning
2 new in second picture
3 only shows up in the last picture

Earlier work by Shuhan Lin in our lab had indicated that these defects also form after chemical etching of the silicon surface, arguing for a mechanism involving instabilities in the surface oxidation front rather than anything specific to ion-milling alone. This has been supported by high resolution imaging of these defects down <001>, and analysis of defect contrast in the presence of thickness fringes. These earlier observations suggested that the defects had depths comparable to their widths, in some cases evidenced slight in-plane faceting along (110), and themselves evidence contrast like that of an amorphous thermal oxide. One thing we had not done was to compare *rates* of defect formation with chemical versus ion-mechanical thinning. If the etching process hydrogen passivated the silicon surface against oxidation, the rate of defect formation might have been less for the chemically thinned surface. However, if ion-mill damage layer (typically 5nm in thickness) served to retard diffusion of the oxidation front against the now buried single crystal silicon surface, the defect formation process might be slower in the ion milling case.

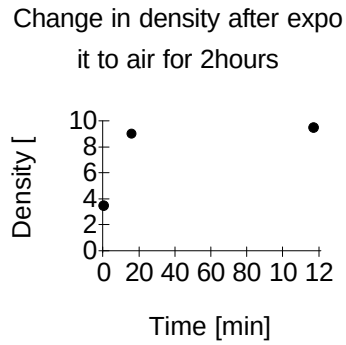
The preparation of the specimen with chemical etching lead to very high densities right after putting it in the microscope, even though contact with air is very short. Subsequent observation suggested that the defect densities were not changing in the microscope, suggesting that the surface defect-formation reaction was already complete. MORE DOCUMENTATION NEEDED. Hence it appears that in chemically etched silicon, the acid oxidation front itself, or the absence of a damage layer when the surface is exposed to air after etching, may give us an array of surface defects already in place even when the specimen is promptly placed into the microscope. By comparison, the ion milling process may put in place a diffusion barrier (the ion-mill damage layer) that (i) adsorbs oxygen from the air, but then (ii) retards it's diffusion to the reaction layer at the top of

the undamaged silicon. This will allow the formation of defects in vacuo, after air exposure of the specimen, until adsorbed oxygen is used up

The density versus time measurement on a second specimen confirms the observations above, and shows a rapid increase of the defects at the beginning, which slows down after seven hours (420 minute mark on Fig. 2). Note in Fig. 2 that the time axis to the right of the 800 minute mark is labeled in units of 10 rather than 1 minute. Saturation is not detectable during a period of twenty-six and half-hours, which leads to the presumption that the growth of the defects is not a process that will only occur in the first few hours after ion milling. However, the reduction in growth rate suggests that the oxygen concentration gradients driving diffusion of oxygen to the reaction front may be showing signs of depletion, while the surface is held in the microscope vacuum. In that context, the bend in the rate curve at 420 minutes may relate to the thickness of the damage layer. Once the damage layer above the defect site is depleted of oxygen, in-layer diffusion can only draw from a region which grows laterally in two dimensions rather than three.



As shown in Fig. 3 below, exposing the wafer to air can increase the density significantly. Also formation of the defects is much faster. (Again note the change in time units along the x-axis. The y-axis is in units of ----/cm^2.) This same pattern of behavior was also observed with the first specimen. From these experiments, it seems that saturation is fulfilled already after being in contact with air for few hours. This suggests that one should minimize the time the wafer is exposed to air, if interested in looking for bulk defects smaller than 10Å. Also, of course, this is consistent the possibility of. concentration depletion in vacuo, when .defects are grown in the microscope. This is because diffusion coefficients for this “buried layer reaction” are unlikely to increase when the specimen is brought into air. Nonetheless the unlimited availability of oxygen at the surface seems to allow the reaction to move to “saturation” in only two hours.



In summary, this report extends earlier work in this lab on spontaneously forming defects in the 10nm size range, which may signal a previously unrecognized instability in the surface oxidation of silicon. Although the nucleation of defects may have some connection to the things like vacancy clusters in the underlying silicon, our preliminary look at specimens (and prep techniques) going back well into the 1980's suggests that this is probably not a phenomenon isolated to one type of single crystal silicon. We also don't know if it is preferential to (001) surfaces, although the formation of these defects under an ion milling damage layer suggests that the details of the surface may be irrelevant.

One obvious question: If this surface oxidation instability is present in specimens other than those prepared for the TEM, "shouldn't it have been seen elsewhere". The answer to this question may be tied up with the nature of surface oxidation itself. The defects are buried beneath the silicon surface, and it is well known that native oxidation proceeds so gently that 0.13nm steps are preserved for weeks in air exposed specimens, even after the oxide is more than a nm thick. Our atomic force work on these specimens confirms little or no alteration of surface topography in association with these defects. Hence they may not be detectable individually at the surface, although they may contribute to visible light scattering, given the transparency of the oxide in the visible! The next generation of imaging ion probes (like Ernst's "nano-SIMS" at WU) might allow their detection in oxygen isotope image maps. The reasons we have ignored them in TEM images so far: They are quite small compared to defects we usually look for, and they have little or no strain fields of the sort typical of bulk defects. Prior to our "closer look" in recent days, we have generally chalked them up as "possible milling damage" not considered further.

Another result: Ion-milled specimens may be best for studying these defects, because we can slow down and observe the growth process in action. Questions relating to the future relevance of these defects include: Does the density of these defects depend on V/I ratios across a wafer? How does the kinetics of their growth vary with milling angle, energy, etc. Do the abundances of these defects vary with silicon doping and orientation type? Are the abundances by ion-milling similar to those after etching, or polishing? (For example, single side milled specimens should allow a look for these defects beneath

a polished wafer surface.) Once we find specimens with noticeably different defect densities, can we see effects in the Tencor or other optical scattering instruments related thereto?

Lastly, in context of the project first inspiring this work, can we suppress the growth of these defects sufficiently to detect the bulk MDZ defects that Jeff was interested in a look at originally? A quick answer: the highest bulk defect counts in Jeff's specimens (e.g. 7x10^9/cc) will yield about 0.001 defects per um^2 in the TEM. Our first attempts to suppress their formation (by running down the hall with the specimen in air) gave us surface defect number densities on the order of 1 per um^2. We maybe able to do significantly better than this with argon or nitrogen backfill, glove bags, and/or transfer stages. In the meantime, a look at Jeff's defects after they've been "grown" (e.g. those counted in the BMD numbers he provided) might be helpful in telling us precisely what to look for, as we begin to sort the wheat from the chaff.

References

1. U. Bangert, P.J. Goodhew, C. Jeynes and I.H. Wilson: *J. Phys. D: Appl. Phys.* **19** (1986) 589