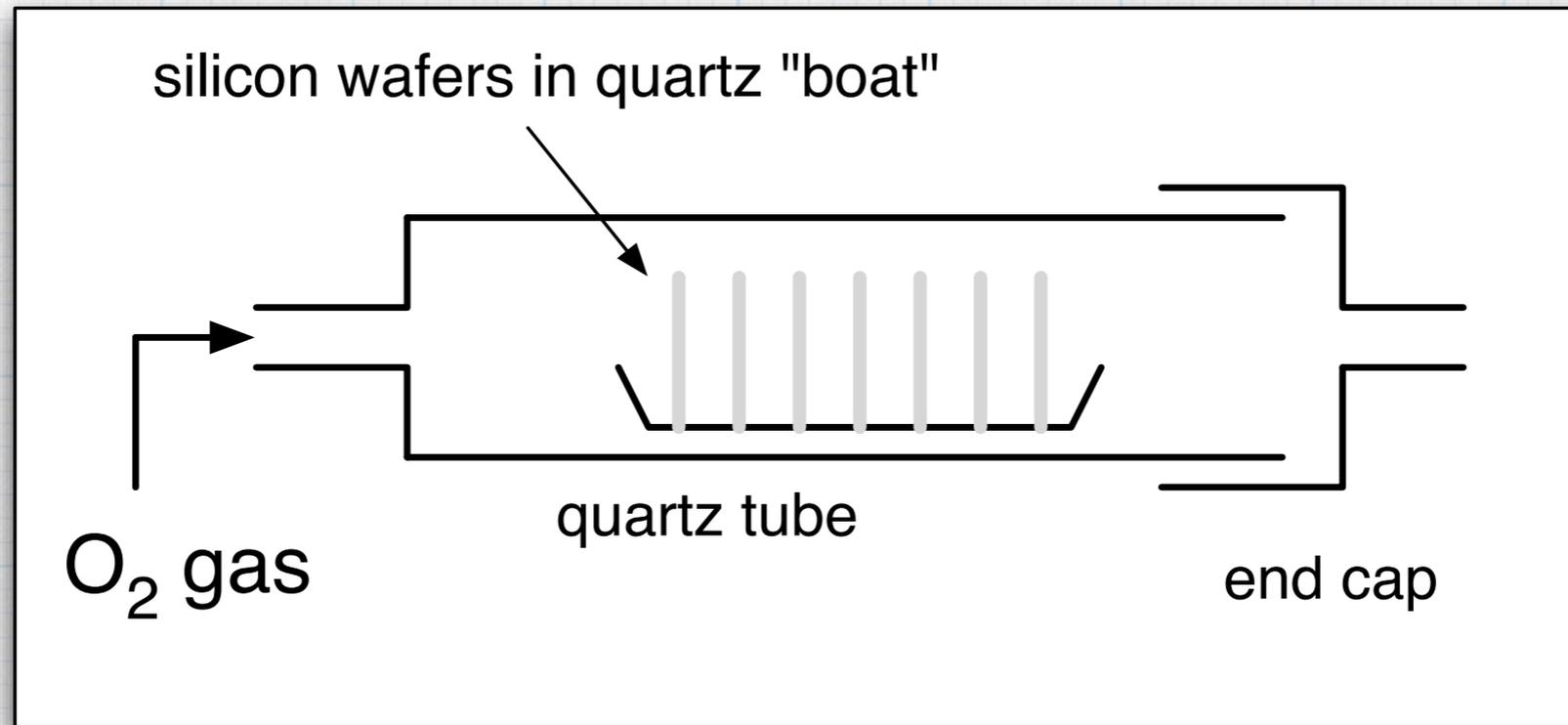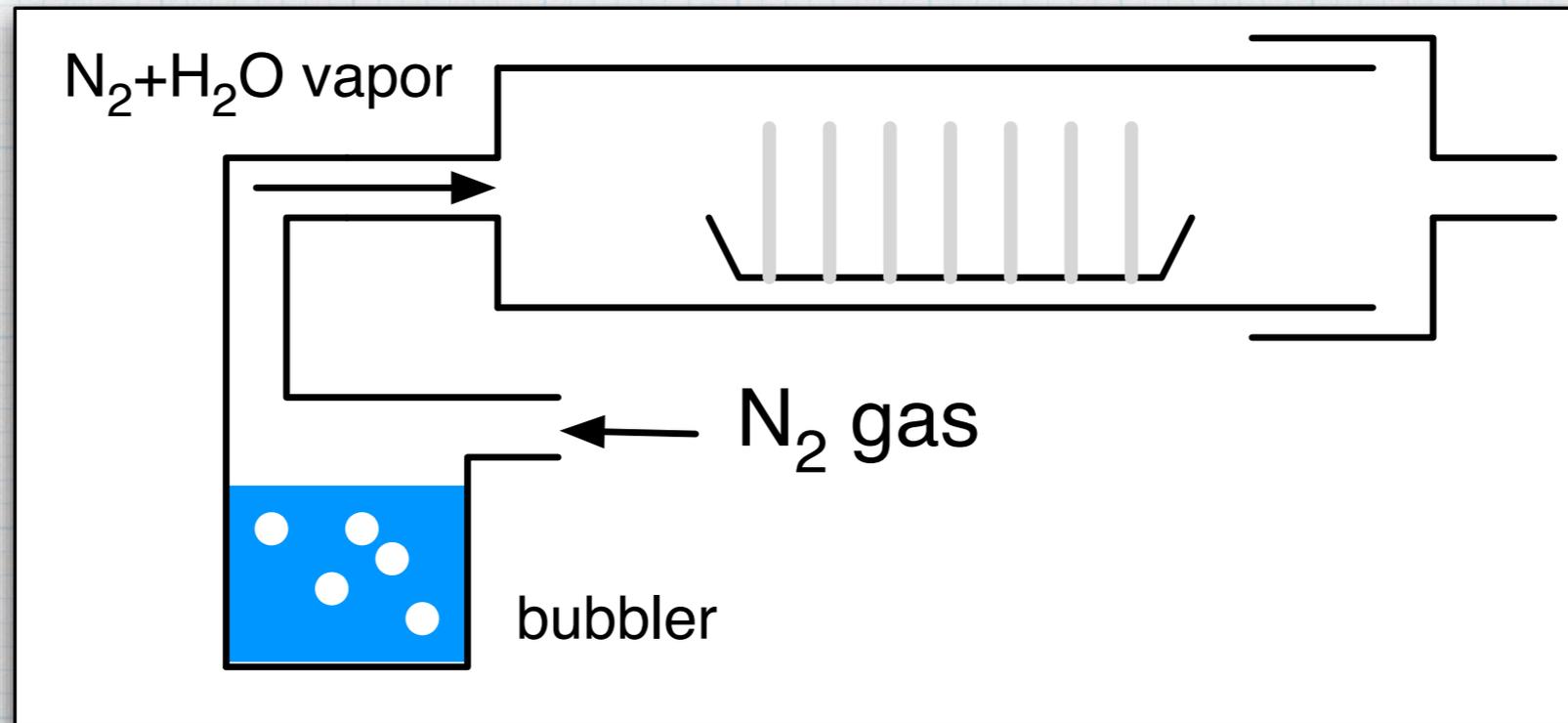# More on oxidation

- Oxidation systems

- Measuring oxide thickness

- Substrate orientation

- Thin oxides

- Oxide quality

- Si/SiO$_2$ interface

- Hafnium oxide

Oxidation systems

Dry oxidation

silicon wafers in quartz "boat"

quartz tube

O_2 gas

end cap

Wet oxidation
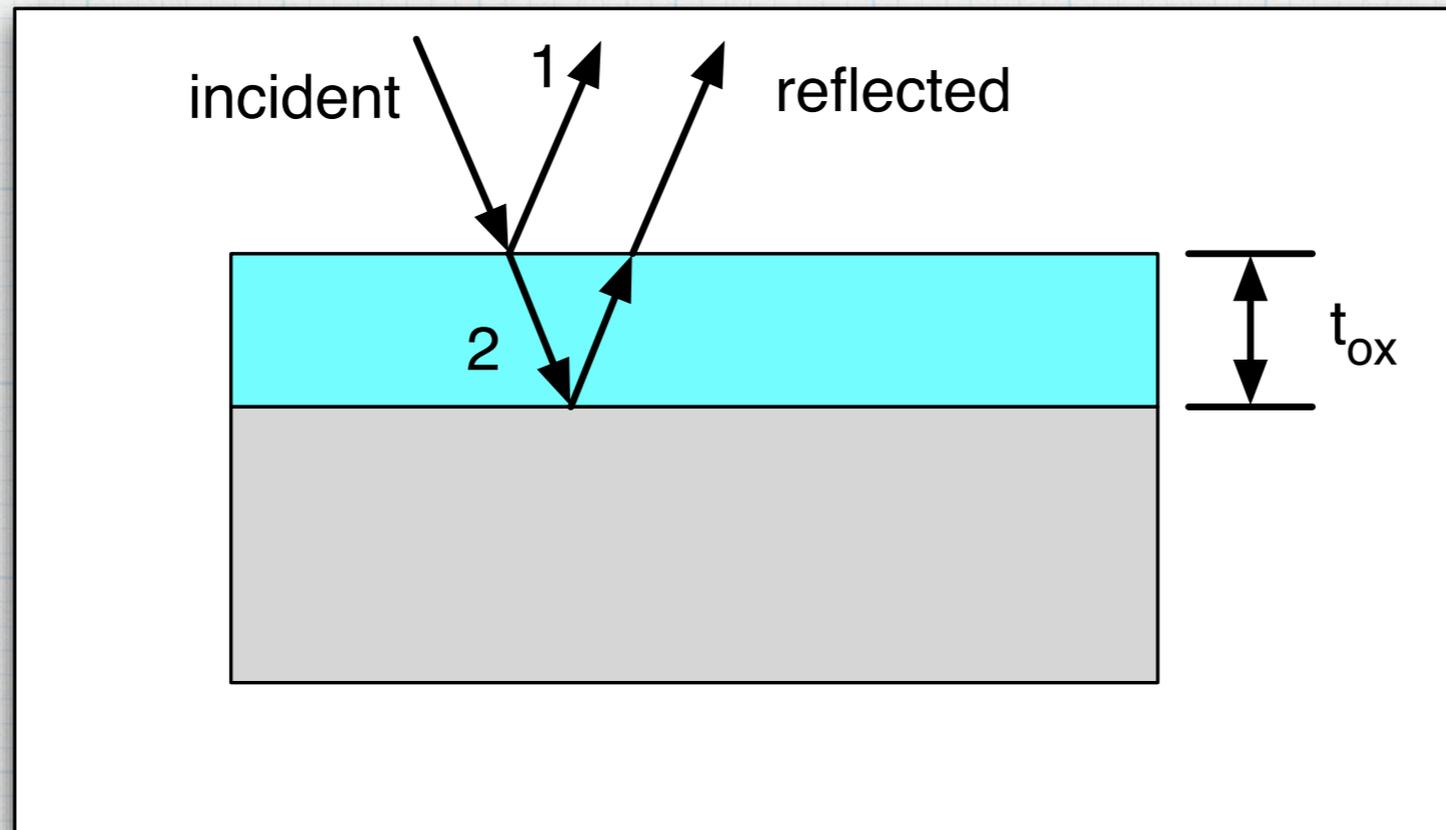
N_2+H_2O vapor

N_2 gas

bubbler

Water vapor can also be formed directly from H_2 and O_2 using a pyrolytic torch.

Measuring oxides

- Optical
    - color chart
    - reflectance spectrum
    - ellipsometry

- Mechanical
    - profilometer

- Electrical
    - capacitance
    - leakage currents

Optical reflection

Shine light on the surface of the wafer and measure the amount of reflected light.

Constructive interference of the reflections when the path length difference is equal to one wavelength (or multiple of wavelengths). Assuming normal incidence, there will be a strong reflection when $\lambda_o/n = 2t_{ox}$. Since most of the other colors are interfering (at least somewhat) destructively, the peak wavelength will pre-dominate, so that the oxide appears to have a very distinct color. The oxide is transparent (colorless), but the effect of the interference is to make it appear to have a specific color.

0.05	Tan	0.48	Blue violet	1.00	Carnation pink
0.07	Brown	0.49	Blue	1.02	Violet red
0.10	Dark violet to dark red	0.50	Blue green	1.05	Red violet
0.12	Royal blue	0.52	Green (broad)	1.06	Violet
0.15	Light blue to metallic blue	0.54	Yellow green	1.07	Blue violet
0.17	Metallic to light yellow green	0.56	Green yellow	1.10	Green
0.20	Light yellow or gold	0.57	Yellow to "yellowish"	1.11	Yellow green
0.22	Gold with slight yellow	0.58	Light orange or yellow to pink	1.12	Green
0.25	Orange to melon	0.60	Carnation pink	1.11	Yellow green
0.27	Red violet	0.63	Violet red	1.12	Green
0.30	Blue to violet blue	0.68	"Bluish"	1.18	Violet
0.31	Blue	0.72	Blue green to green	1.19	Red violet
0.32	Blue to blue green	0.77	"Yellowish"	1.21	Violet red
0.34	Light green	0.80	Orange	1.24	Carnation pink to salmon
0.35	Green to yellow green	0.82	Salmon	1.25	Orange
0.36	Yellow green	0.85	Dull, light red violet	1.28	"Yellowish"
0.37	Green yellow	0.86	Violet	1.32	Sky blue to green blue
0.39	Yellow	0.87	Blue violet	1.40	Orange
0.41	Light orange	0.89	Blue	1.45	Violet
0.42	Carnation pink	0.92	Blue green	1.46	Blue violet
0.44	Violet red	0.95	Dull yellow green	1.50	Blue
0.46	Red violet	0.97	Yellow to "yellowish"	1.54	Blue
0.47	Violet	0.99	Orange		

Oxide Thickness [Å]	COLOR	COLOR CODE	Color and Comments
500		D2B48C	Tan
750		A52A2A	Brown
1000		B32F79	Dark Violet to red violet
1250		2E73F3	Royal blue
1500		ADD8E6	Light blue to metallic blue
1750		D9ECB3	Metallic to very light yellow-green
2000		F9F9C8	Light gold or yellow slightly metallic
2250		DAA520	Gold with slight yellow-orange
2500		F6853D	Orange to Melon
2750		B32F79	Red-Violet
3000		5D3694	Blue to violet-blue
3100		0000FF	Blue
3250		0083AE	Blue to blue-green
3450		00FF00	Light green
3500		84D82E	Green to yellow-green
3650		84C82E	Yellow-green
3750		E2DE2B	Green-yellow
3900		FFFF00	Yellow.
4120		FFB500	Light orange
4260		FA7FC1	Carnation pink
4430		E82362	Violet-red
4650		B32F79	Red-violet
4760		EE82EE	Violet
4800		5D3694	Blue Violet
4930		0000FF	Blue
5020		008080	Blue-green
5200		008846	Green (Broad)
5400		9ACD32	Yellow-green
5600		ADFF2F	Green-yellow
5740		FFFFD2	Yellow to Yellowish (not yellow but is in the position where yellow is to be expected. At times is appears to be light creamy gray or metallic)
5850		FFDE93	Light orange or yellow to pink borderline
6000		FA7FC1	Carnation pink
6300		EE82EE	Violet-red
6800		AE82FF	Bluish (Not blue but borderline between violet and blue-green. It appears more like a Mixture between violet-red and blue-green and over-all looks grayish)
7200		00A080	Blue-green to green (quite broad)
7700		FFFF8C	Yellowish
8000		FFA500	Orange (rather broad for orange)
8200		FA8072	Salmon
8500		B32F79	Dull, light red-violet
8600		EE82EE	Violet
8700		5D3694	Blue-violet
8900		0000FF	Blue
9200		0083AE	Blue-green
9500		84C82E	Dull yellow-green
9700		FFFF00	Yellow to Yellowish
9900		F3770C	Orange
10000		FA7FC1	Carnation Pink

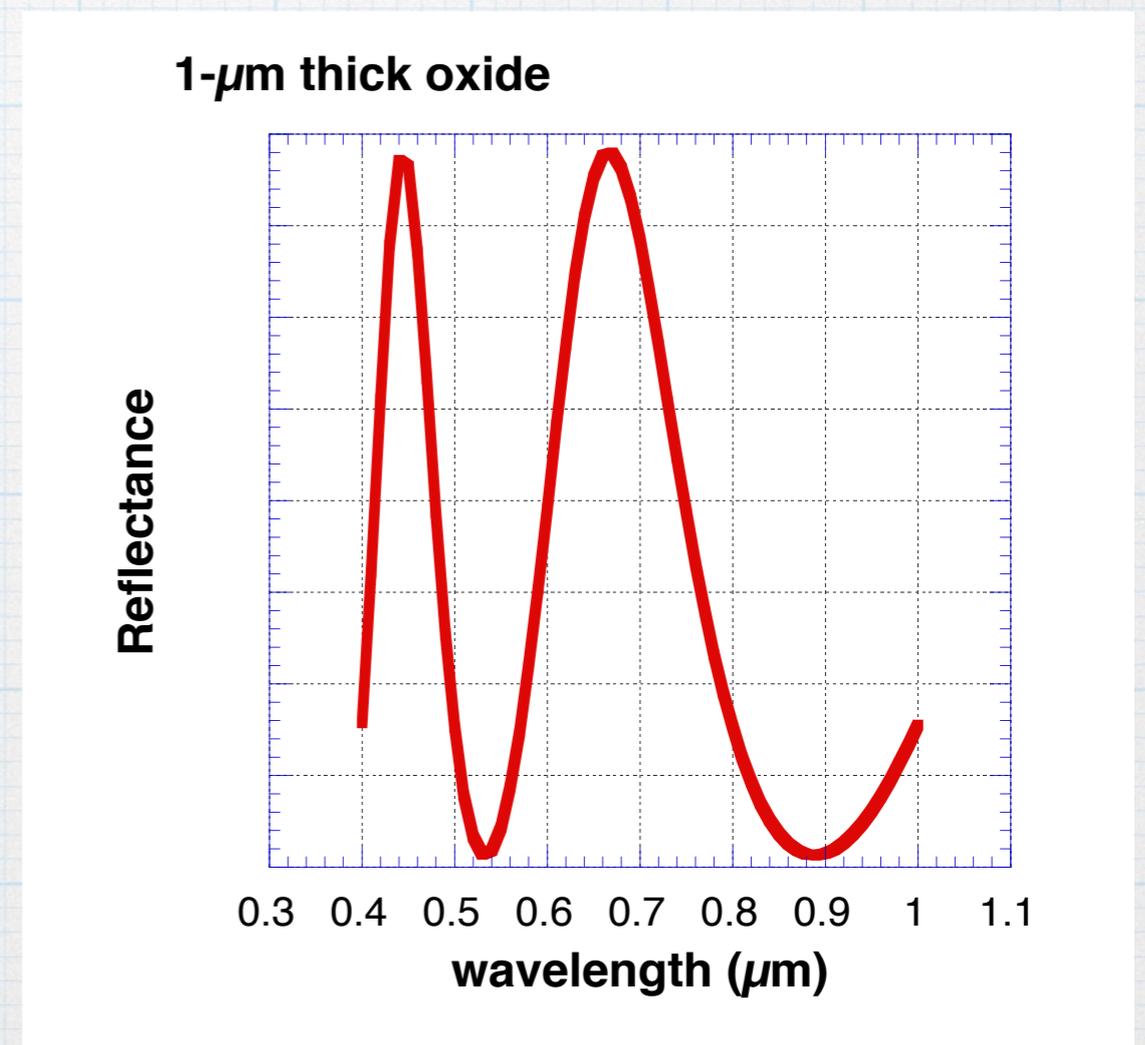http://www.cleanroom.byu.edu/color_chart.phtml

A better method – reflectance spectroscopy

Instead of looking at a single point, take a whole spectrum and fit the data to a model of the reflectance. For a simple one layer system, the total reflectance has the following form (see EE 438)

$$R = 1 - \frac{(t_1 t_2)^2}{1 - 2r_1 r_2 \cos\left(\frac{4\pi t_{ox}}{\lambda}\right) + (r_1 r_2)^2}$$

where t_1 and t_2 are the transmission coefficients for each interface and r_1 and r_2 are the reflection coefficients.

Filmetrics system does this. Measure the spectrum and then make the equation fit the measured curve by adjusting the value for t_{ox} (and maybe n).

1-µm thick oxide

Reflectance

0.3   0.4   0.5   0.6   0.7   0.8   0.9   1   1.1

wavelength (µm)

Substrate orientation

Previously, we've pointed out that the oxide growth rates given in the Deal-Grove lecture are for (100) surfaces of silicon. Different surfaces show different rates.

The linear reaction rate depends on how many silicon atoms are available for oxidation, so the reaction rate will depend directly on the density of atoms at the silicon surface.

Out of the major crystal surfaces, the (100) surface has the lowest atom density.

The (110) surface has 20% more atoms than (100); (111) has 68% more atoms. For these faces, the linear growth increases proportionally over the (100) rate.

In the IC business, (100)-oriented wafers are used almost exclusively. However, if the wafer is etched, the etch facets may be something other (100), and so the rate enhancement may come into play.

Oxide quality

• The quality of the oxide depends primarily on the density. Since there is some flexibility in how closely the Si-O tetrahedra can be packed, there will be variations in density.

• Increased density manifests itself in terms of higher breakdown fields (important in the gate layer of a MOSFET) and lowered volatility (harder to react with other materials, slower etch rates.)

• If oxide quality is a concern, we need to make the growth conditions conducive to higher density. In general, this means slower growth rates and higher temperatures.

• Thus we expect dry oxidation to give better oxide than wet.

• It is also possible to "anneal" an oxide to increase the density. For example, leave it in the furnace at an elevated temperature for some time.

• Later, we will look at CVD-formed oxides, which are done at much lower temps and higher growth rates. Not surprisingly, these are of much lower quality than thermally grown oxides, although there are other advantages.

Thin oxides

In growing thin oxides, like for the gate of a MOSFET, dry oxidation is typically used, because the slower growth is easier to control the time and the resulting oxide has higher density. However, the Deal-Grove model does not work well in the thin-oxide regime — the grown oxides are always thicker than expected.

Deal and Grove tried to patch up the discrepancy by assuming initial oxides. It became clear that this was not correct, since initial oxides of the necessary thickness to make the theory work were clearly not present.

The explanation is tied up in the atomic-level details of the growth reactions. The exact mechanism has still not been determined.

A mathematical patch that has proven to work reasonably well is modify the growth rate formula of D-G.

D-G:
$$\frac{dt_{ox}}{dt} = \frac{\frac{B}{2}}{t_{ox} + \frac{A}{2}} \approx \frac{B}{A}$$
for thin oxides

$$\frac{dt_{ox}}{dt} = \frac{B}{A} + C \exp\left(-\frac{t_{ox}}{L}\right)$$
ad hoc correction

where C is another Arrhenius-type coefficient and L is a characteristic length over which the enhanced growth occurs.

$$C \approx \left[3.6 \times 10^8 \, \mu m/hr\right] \exp\left(-\frac{2.35eV}{kT}\right)$$

$$L \approx 7 \; nm$$

To find the thickness as a function of time, the above equation would have to be integrated. (See the homework problem.)

The whole of edifice of the integrated circuits industry is built on the fact the $Si-SiO_2$ interface is relatively benign.

The transition from the crystalline silicon lattice to the amorphous oxide network means that there will be lots of broken bonds at the interface. Usually, broken bonds lead to "defect states" or "trap levels" within the bandgap of the of the semiconductor. The defect states can trap electrons, leading to charge build-up at the interface.

While there are certainly defect states at the $Si-SiO_2$ interface, the concentration (number per unit area) is relatively low. For the "as-grown" interface, the density may be around 10^{12} cm^{-3}. This is much lower than other types of semiconductor-insulator interfaces. High trap level densities can lead to "Fermi-level pinning" (see EE 332) where the Fermi level energy "gets stuck" at the trap level energy, making it impossible to modulate carrier concentrations.

The defect density can be lowered even further by annealing the wafers in a hydrogen ambient following the oxidation.

The hydrogen atoms, being very small, diffuse through the oxide easily and attach themselves to the dangling bonds at the interface. (This is known as hydrogenation.) Dangling bonds that have been "healed" in this fashion don't create deep levels.

Annealing in hydrogen gas or forming gas (hydrogen + nitrogen) at 400°C for several minutes can drop interface densities to the range of 10^{11} cm^{-3}.