More on Diffusion

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- Multiple diffusion steps
- Diffusion as nuisance
- Lateral diffusion
- dopant segregation
- masks for dopants
- The diffusion coefficient

Diffusion systems

In general, diffusion systems are similar to oxidation furnaces.

The dopant can be provided in the form of gas, liquid, or solid.

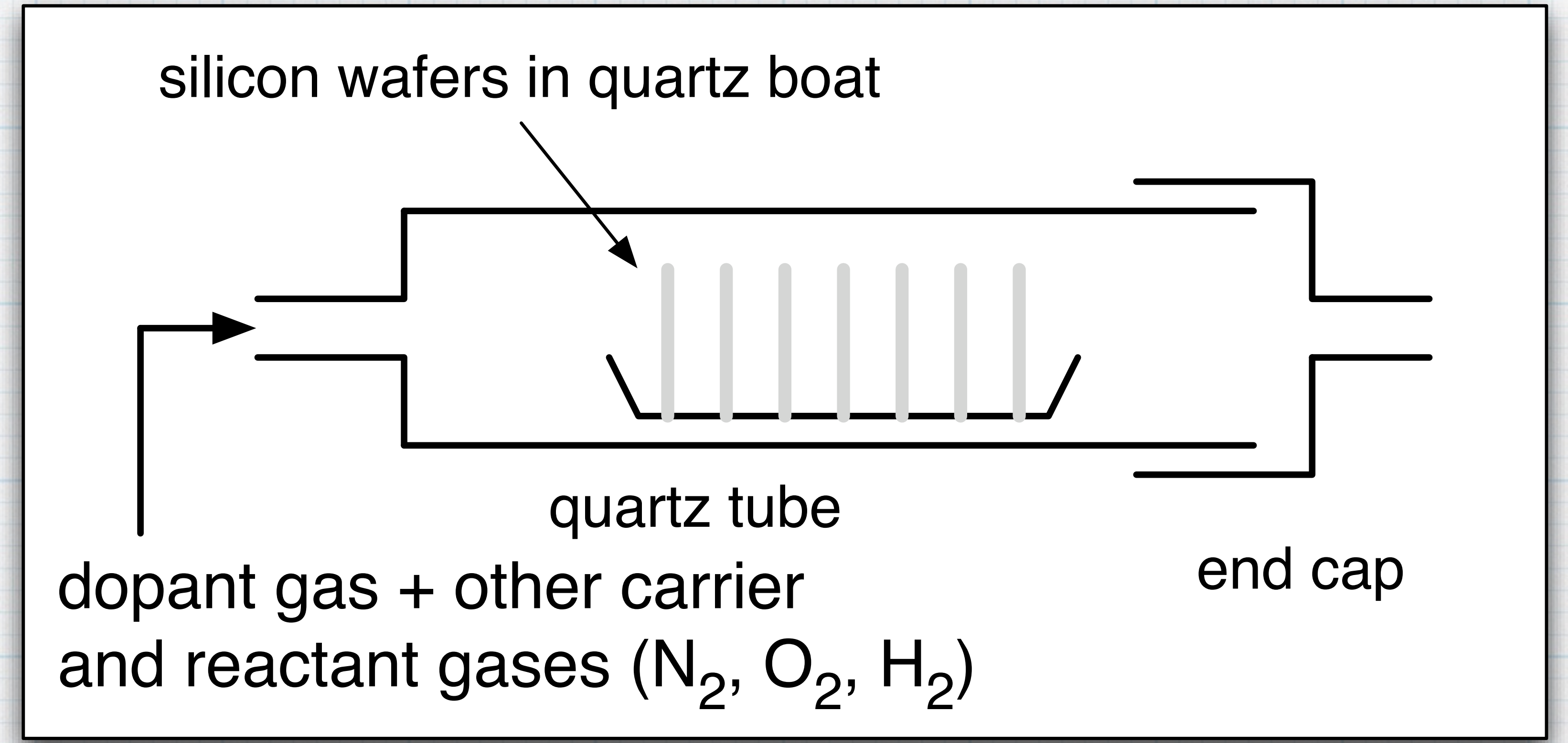
The basic approach is to deposit a glassy layer containing the dopant on the surface of the silicon. A reaction between the glass and the silicon transfers dopant into the silicon.

boron: $2B_2O_3 + 3Si \rightarrow 4B + 3SiO_2$

phosphorus: $2P_2O_5 + 5Si \rightarrow 4P + 5SiO_2$

A potential problem with boron is that excess boron trioxide can cause "boron skin" on the silicon surface. This is difficult to remove by etching. A low-temperature oxidation step can help to break up the boron skin for easier removal. (See the lab information from the manufacturers of the boron source wafers to get more detail.)

Gas sources



boron doping: React diborane with oxygen or carbon dioxide.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$

$$B_2H_6 + 6CO_2 \rightarrow B_6CO + 3H_2O$$

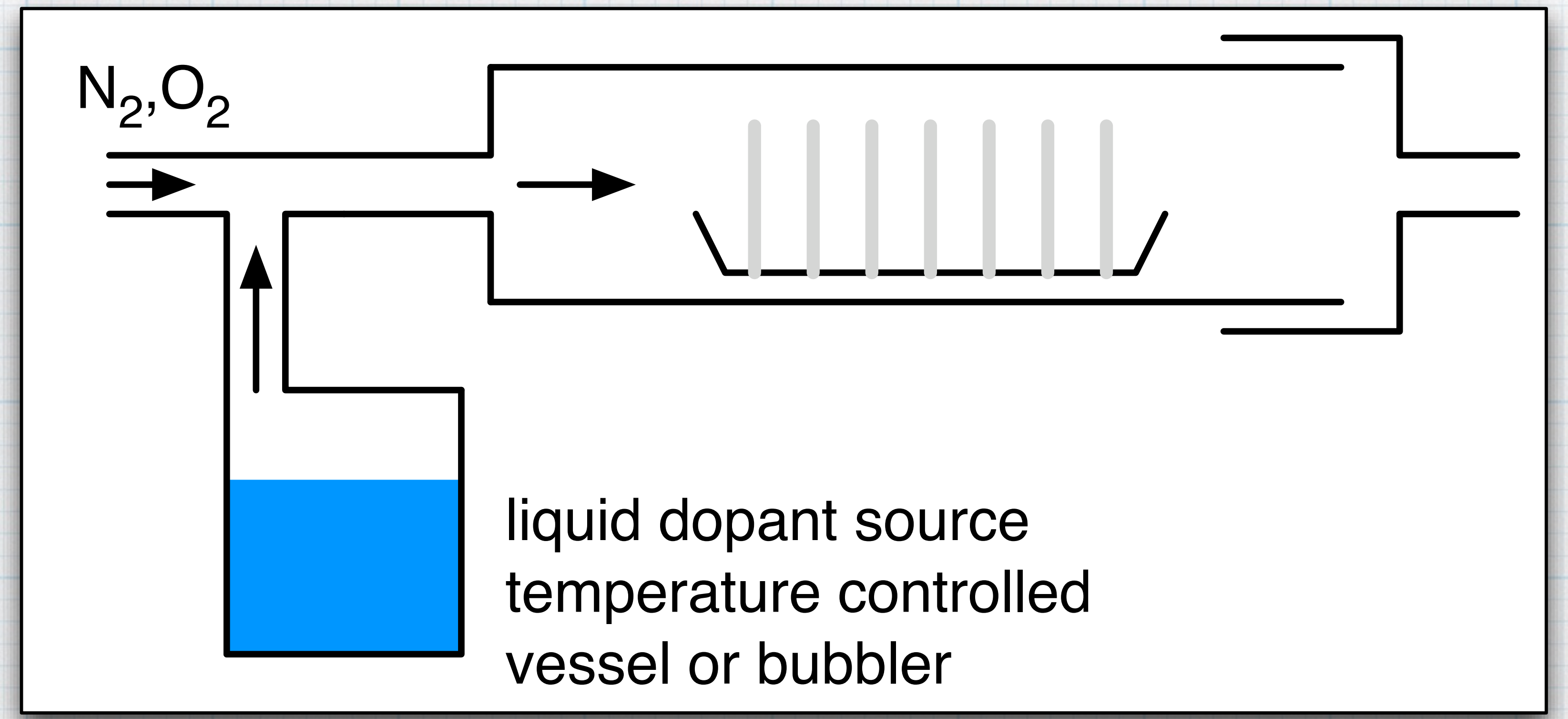
phosphorus doping: React phosphine with oxygen

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$

In either case, the glassy oxide layer is formed on the silicon surface.

The gases used are extremely toxic and special provisions must be used for handling and to clean the gas streams of any unreacted material.

Liquid sources



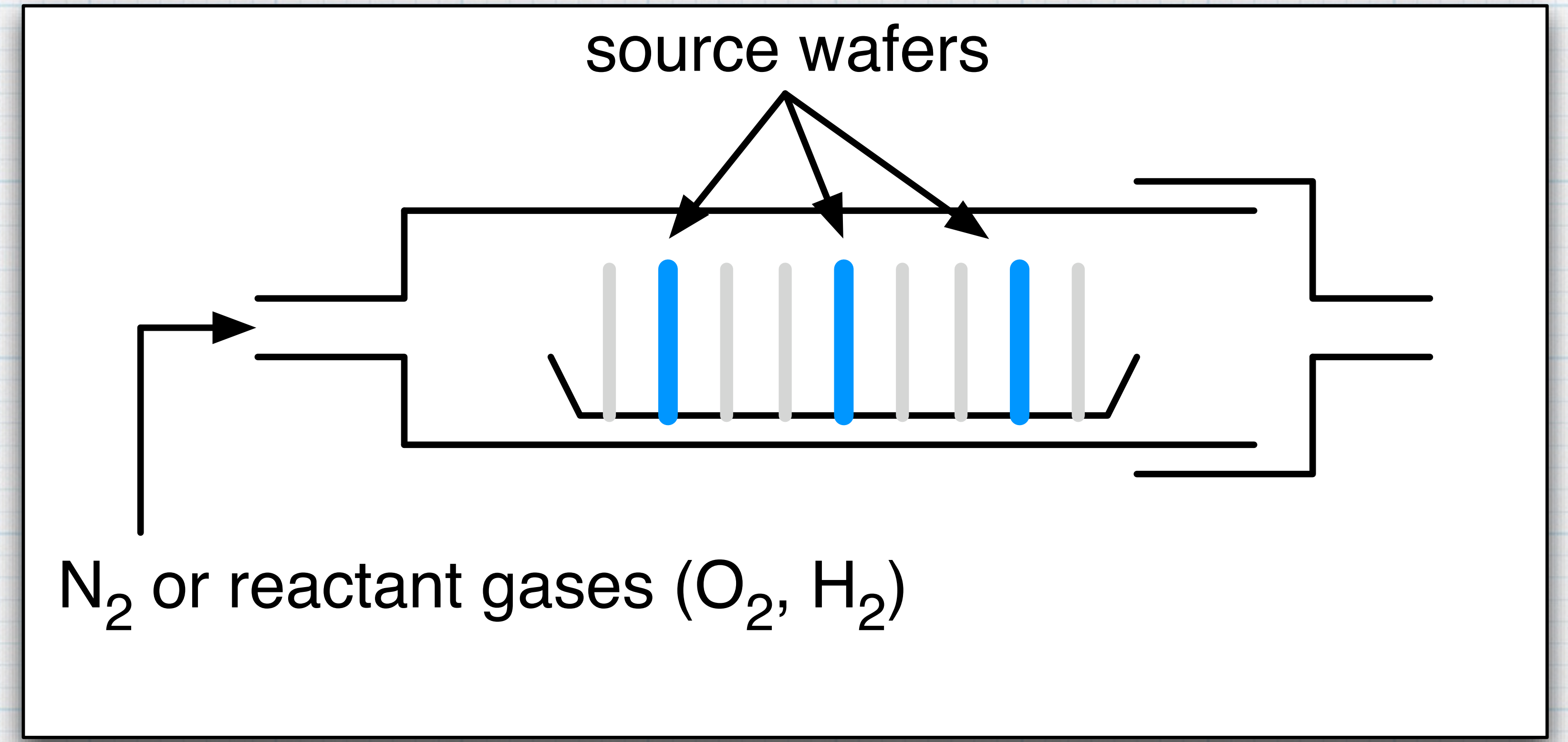
boron doping: react boron tribromide with oxygen

$$4BBr_3 + 3O_2 \rightarrow 2B_2O_3 + 6Br$$

phosphorus doping: react phosphorus oxychloride with oxygen

$$4POCl_3 + 3O_2 \rightarrow 2P_2O_5 + 6Cl_2$$

Solid sources (what we use)



boron: Source wafers are made of nitride (BN). An oxidizing reaction transfers B_2O_3 to silicon surface.

phosphorus: boron nitride/P_2O_5 combination. P_2O_5 transfers directly to the surface of the silicon when the source wafers are heated.

Read the manufacturer's data sheet for details about how this works in practice.

Arsenic

Arsenic has some desirable properties as a dopant. It has high solubility (high concentrations), a relatively low diffusion coefficient, so that once in place it will tend to stay put, and is well-behaved as diffusing species.

However, there are obvious toxicity problems and the various types of As sources that could be used all have various technical problems.

Therefore, the usual way to introduce As is by ion implantation. (More on this later.)

Although other *p*- and *n*-dopants are possible, but B, P, and As are the only ones commonly used today.

Multiple diffusion steps

The drive step may not be done as a single step. It could be broken into 2 or more pieces with different temperatures and times.

This is easily handled by realizing that in starting a diffusion step with an already existing Gaussian profile, the final result will be also be Gaussian. Of course, the profile will be more spread out due to the new diffusion, but it will still have a predictable form.

This means that we can add all of the different drive steps into a single effective drive step by adding up all the Dt-quantities for each individual step.

$$(Dt)_{eff} = D_1 t_1 + D_2 t_2 + D_3 t_3 + \ldots$$
$$= \sum_i D_i t_i$$

Taken to the extreme:

$$(Dt)_{eff} = \int_0^t D dt$$

Diffusion can be a nuisance

In fact, usually we are not intending to do multiple drive steps. Instead, this happens as an artifact of the overall process.

After a particular diffusion step is done, there may be more (maybe many more) subsequent high temperature steps to be completed in the course of a full process. Each one of those will cause further diffusion of the dopants, whether we like it or not.

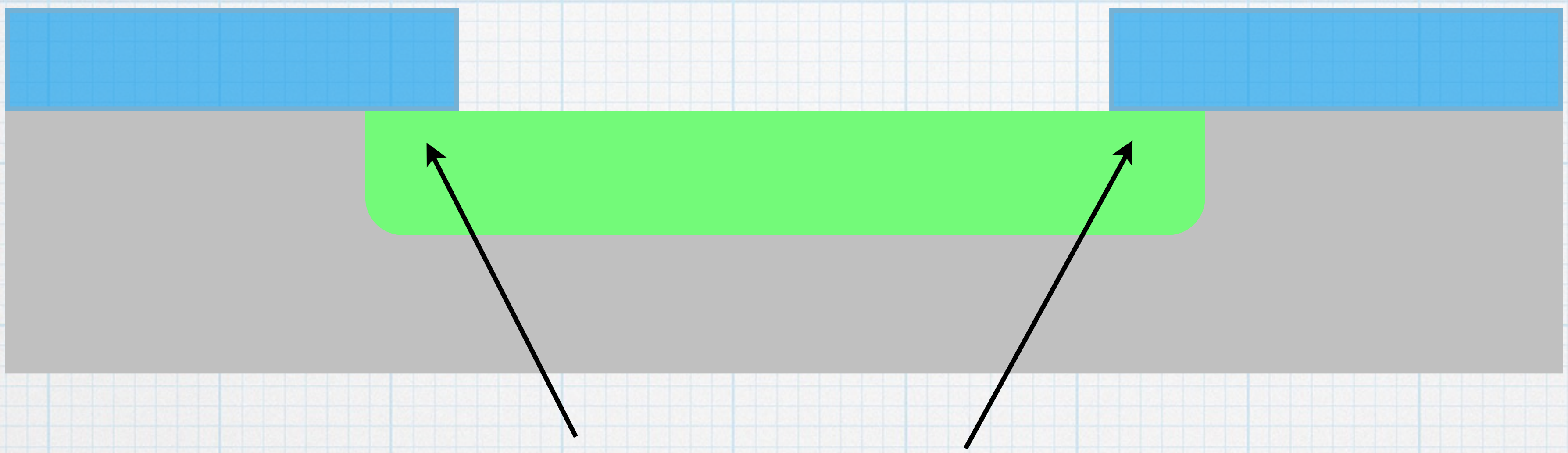
This means that we are “losing control” over your dopant profile, unless you take into account the subsequent changes resulting from the various high temp steps.

This need to pay attention to the entire process is sometimes referred to as managing the “thermal budget” of the process

Much engineering effort is spent in trying to minimize thermal budget, by devising processes that work at lower temperatures.

Lateral diffusion

Of course, diffusion is 3-D, even though we have been treating it as a 1-D problem. This means that dopant will diffuse sideways underneath the edges of a masking layer.

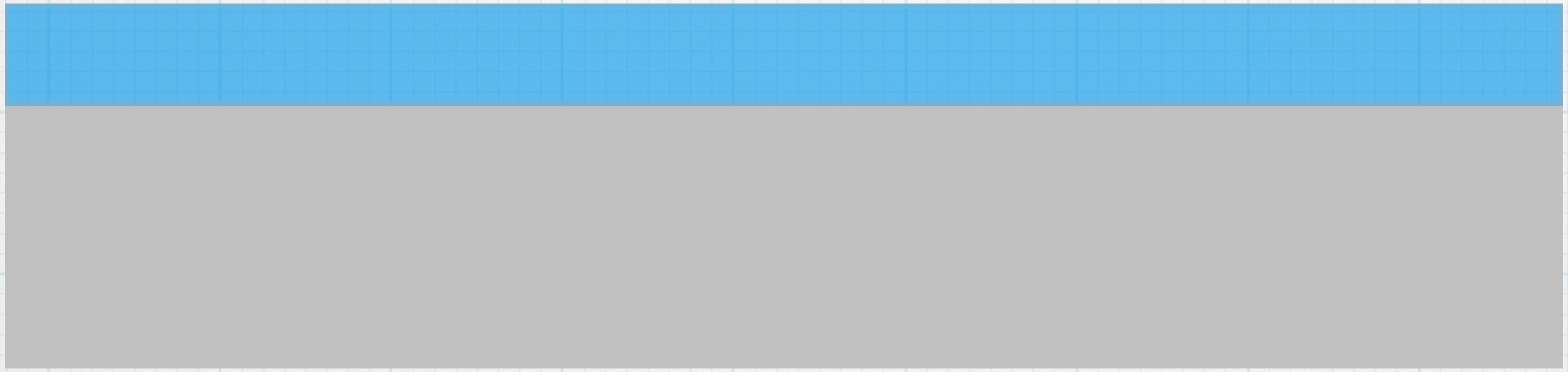


lateral diffusion allows dopant to "leak" under mask edges.

We can get an accurate prediction of the lateral diffusion by solving a 2-D diffusion equation.

Intuitively, we expect that the lateral diffusion is about the same as the junction depth, and this gives a simple "rule of thumb".

The combination of undercutting during etching and lateral diffusion can make patterns much bigger than planned.



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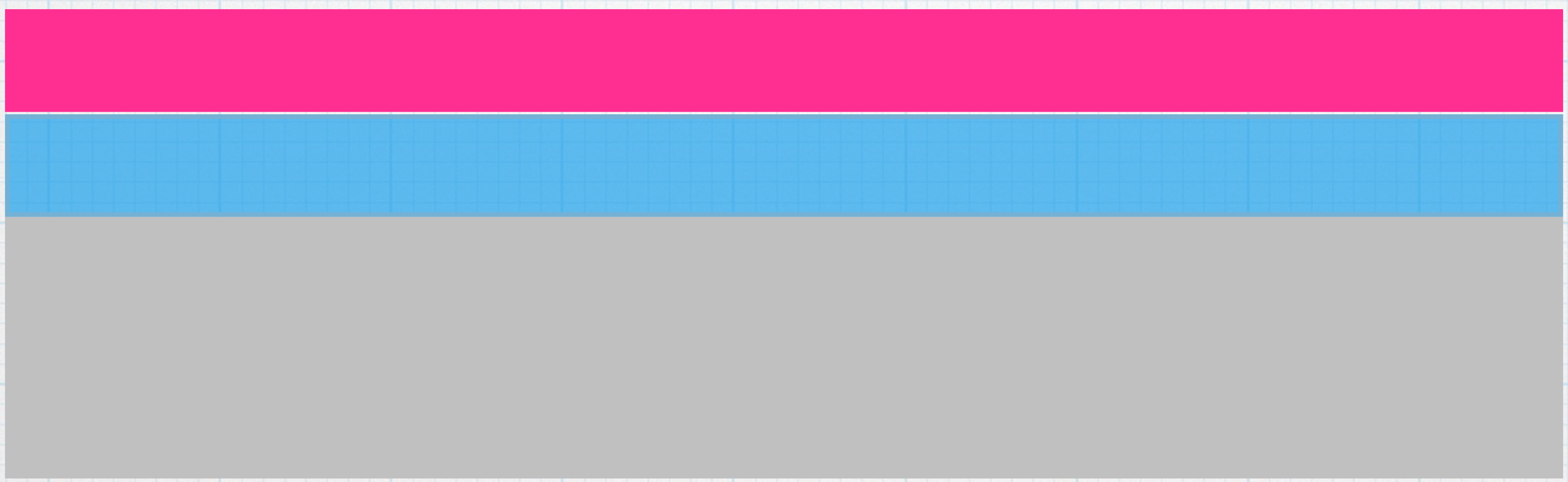

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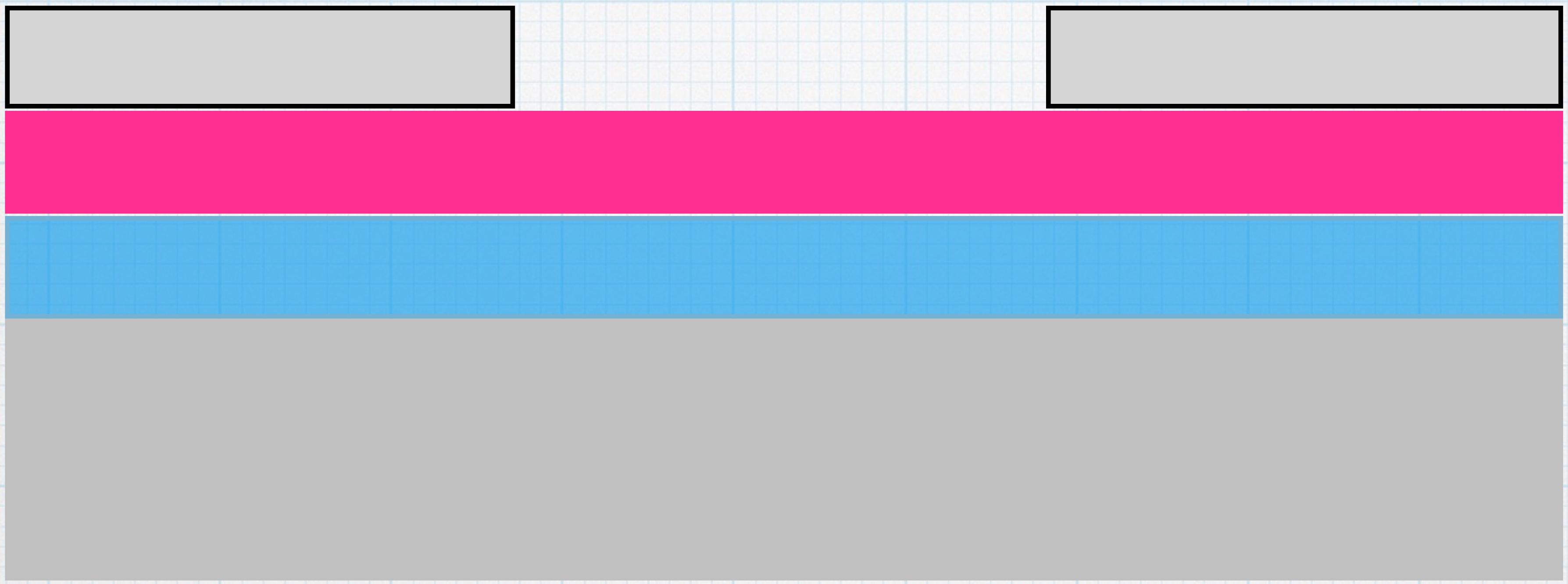

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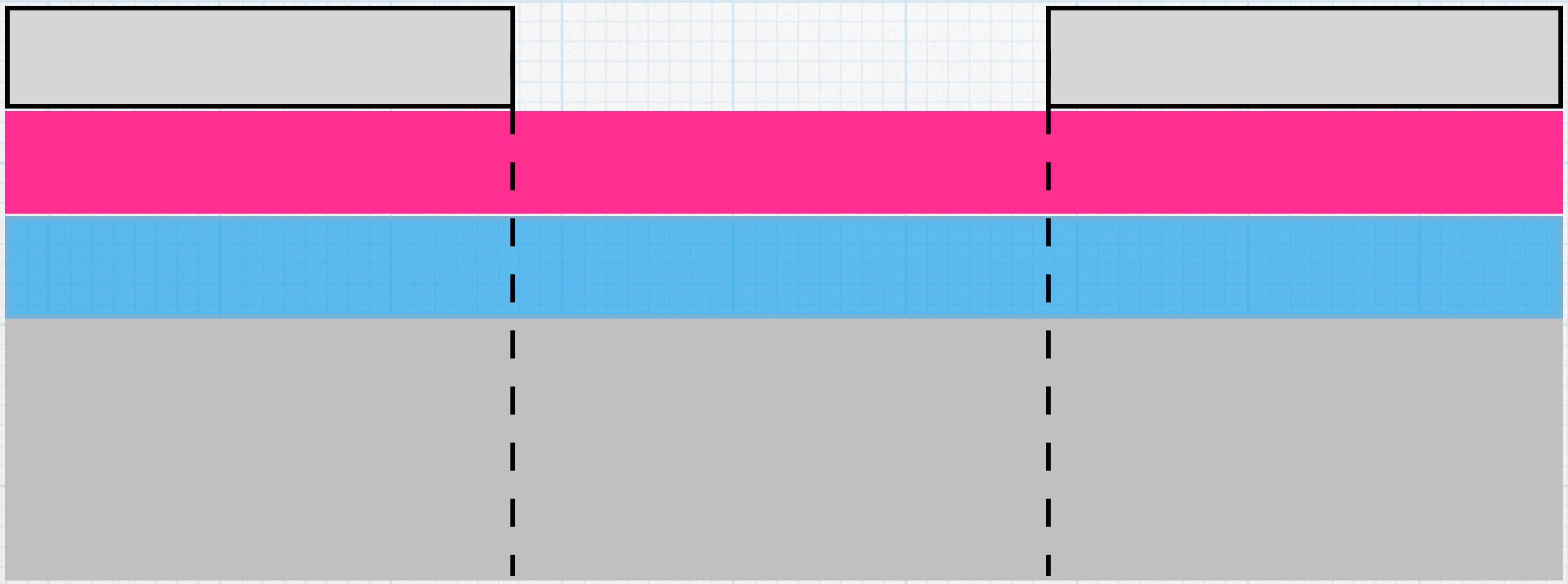

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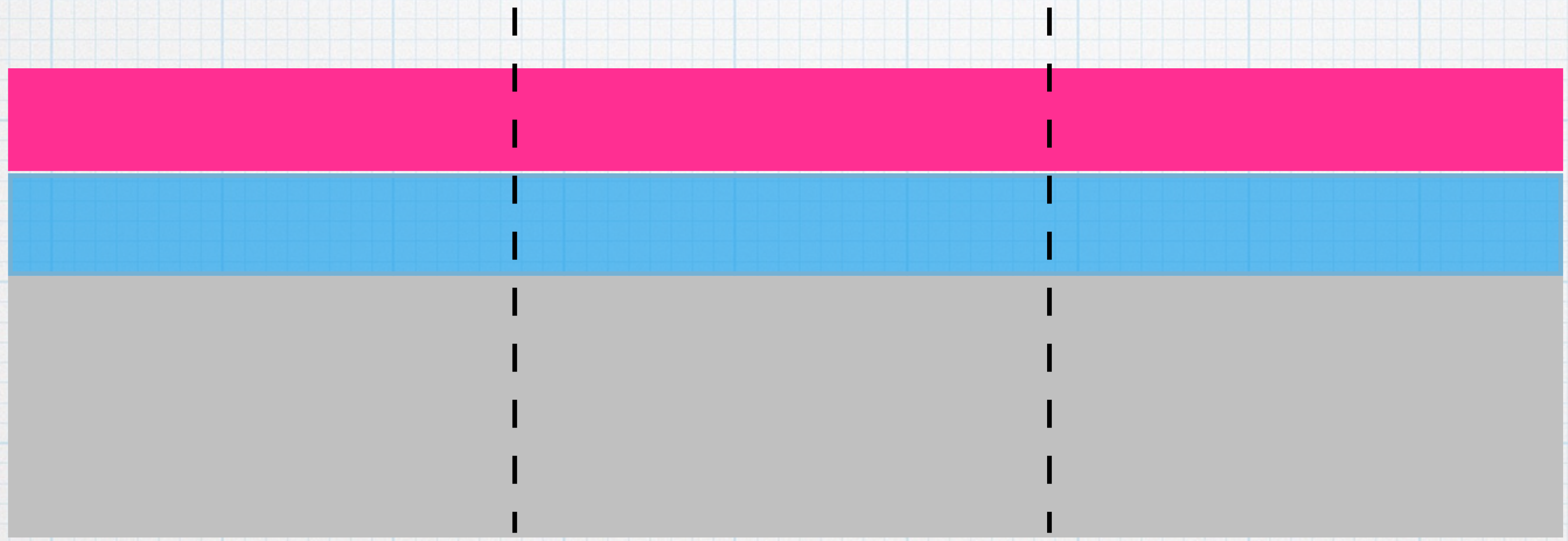

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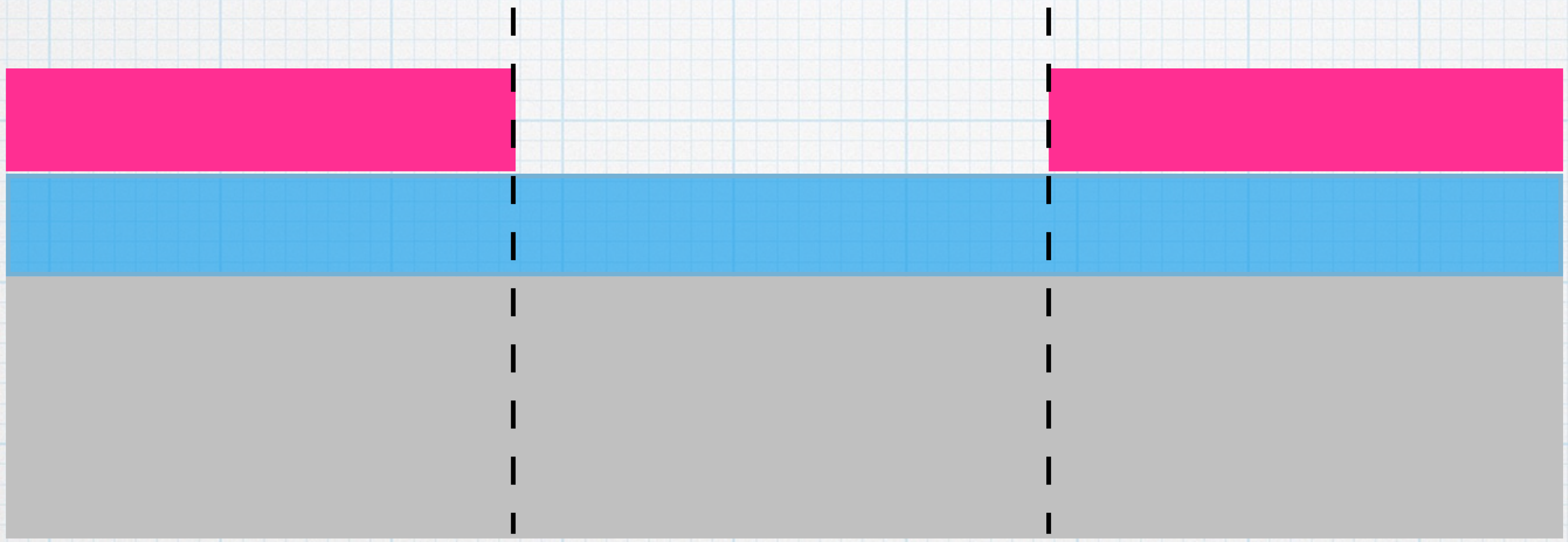

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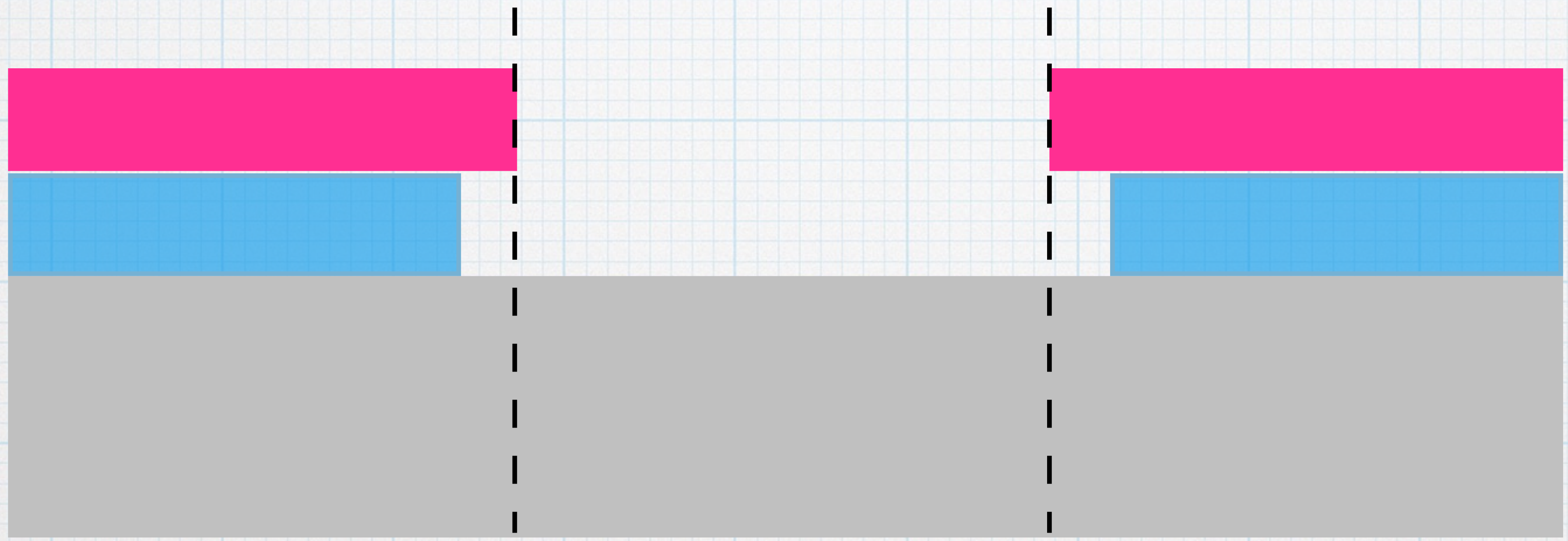

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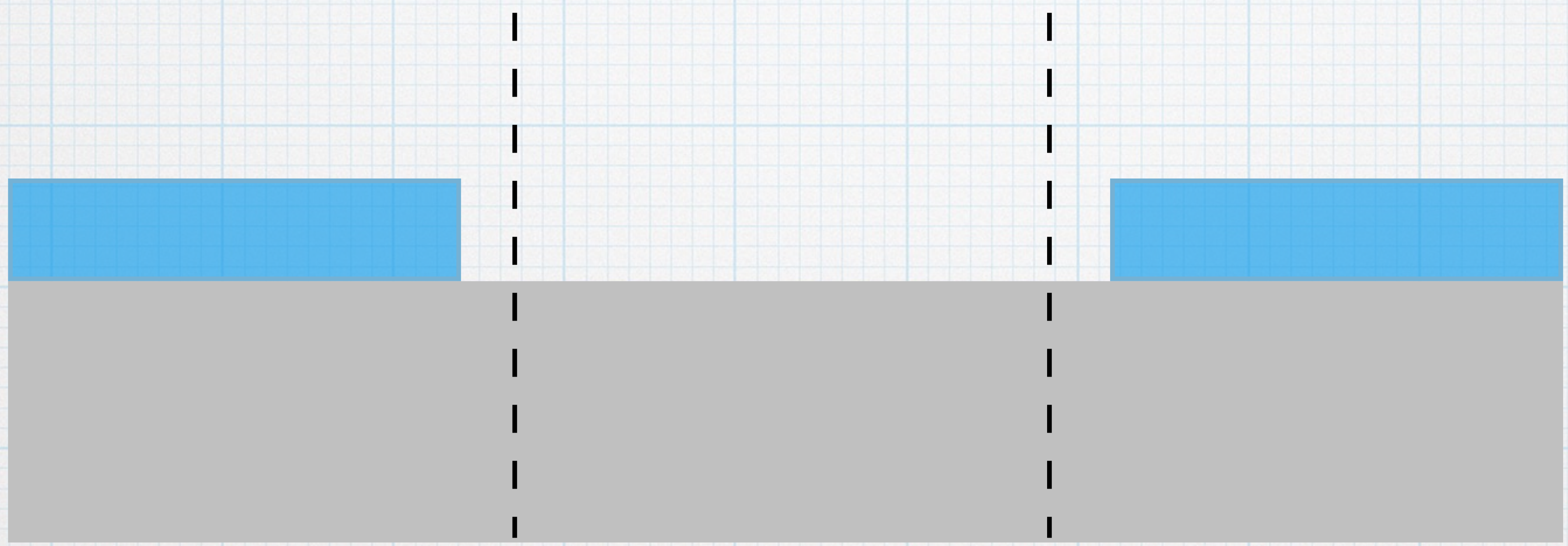

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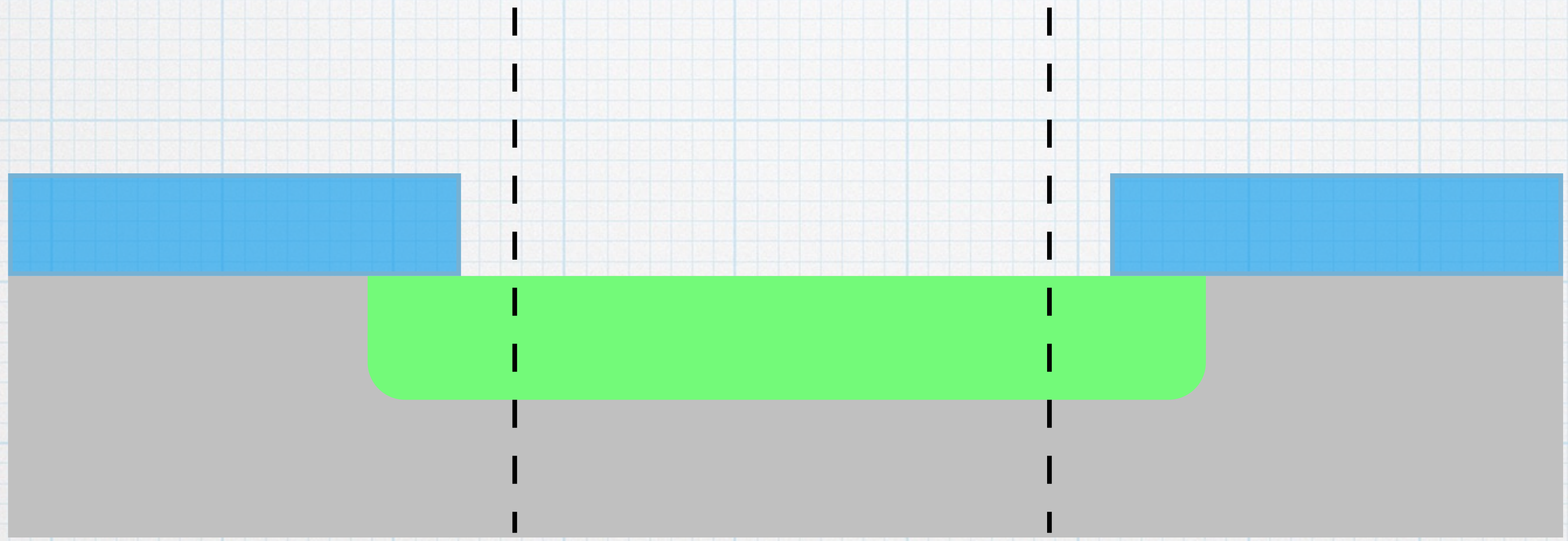


Masking

As discussed earlier, one of the important uses of silicon dioxide is as a mask for dopants.

The key to effective masking is that the dopant have a very low diffusivity in the oxide. This is certainly true for B, P, and As. It is not true for Al and Ga and is the reason that these elements not commonly used as dopant.

(Special note: If boron diffusion is done in the presence of hydrogen, the boron diffusivity in SiO_2 is greatly enhanced, to the point that it is no longer effectively masked by SiO_2. So you should be careful not to do boron depositions while growing wet oxides, since H_2 is a by-product of the wet oxidation process.)

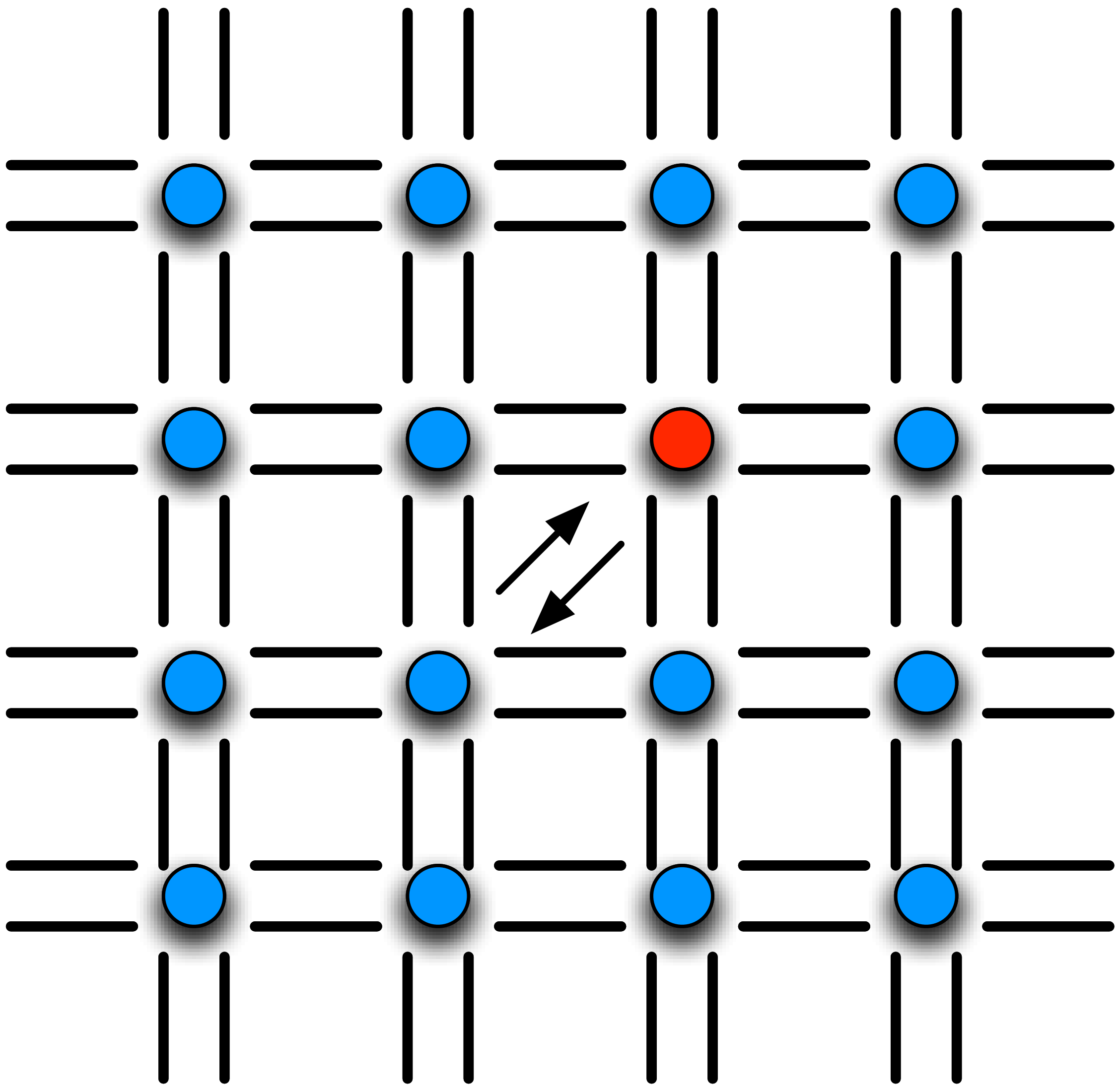
One can define a minimum thickness of oxide needed for effective masking. (For example, see figure 3.10 in Jaeger.) Our CyMOS rule-of-thumb is that 0.25 μm is always adequate.

Substitutional diffusion

We have treated the diffusion coefficient for the various dopants as a simple Arrhenius constant. In many cases, this is an over-simplification. Consider the diffusion process on the microscopic level.

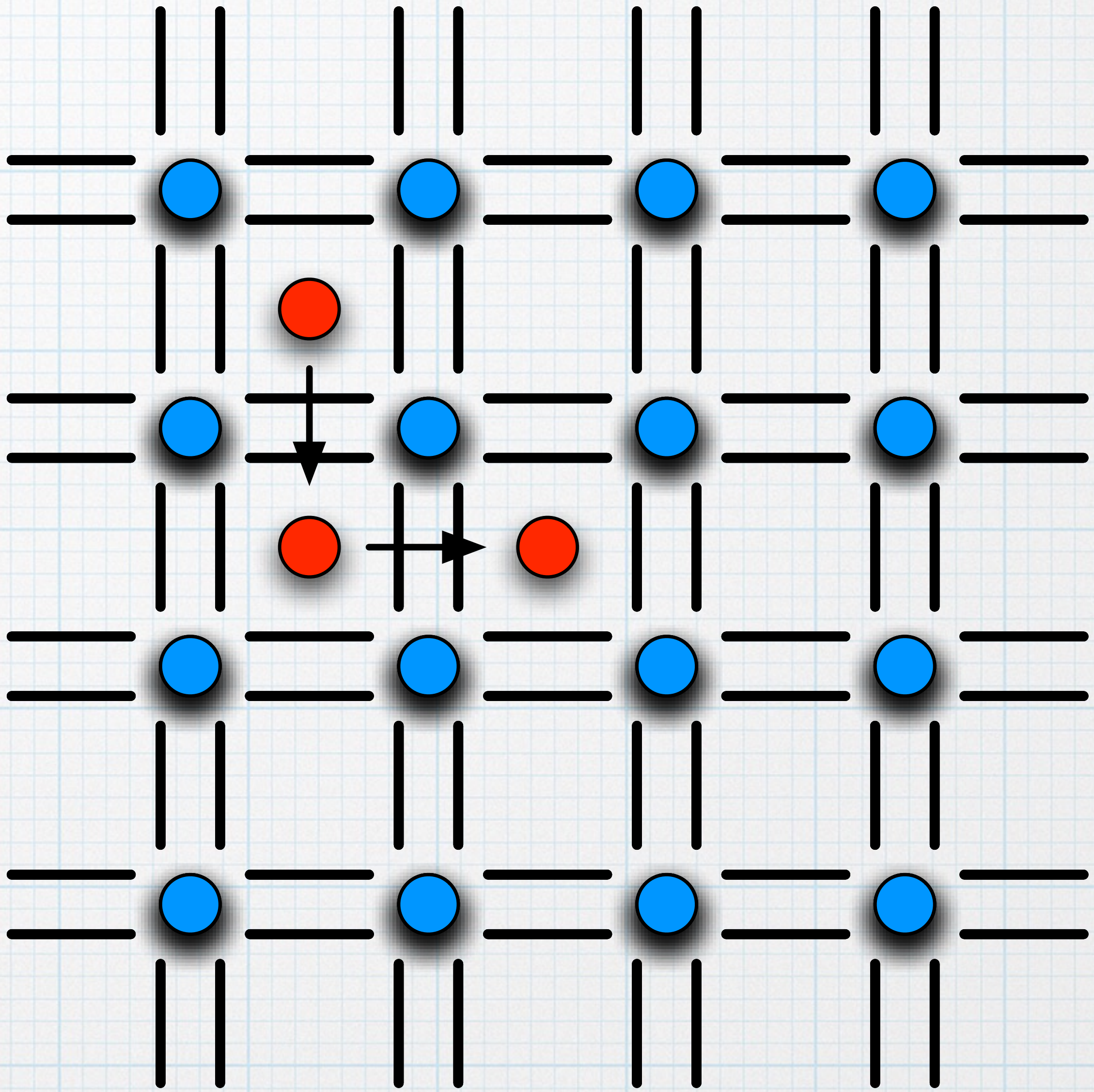
Impurity atoms substitute for silicon atoms in the lattice. The activation energy in the diffusion coefficient expression is an indication of the energy needed for the swap.

$$D_S = D_{OS} \exp\left(-\frac{E_{AS}}{k_B T}\right)$$



Interstitial diffusion

Impurity atoms move by squeezing into the empty spots (interstices) in the lattice. The energy needed to make this move can be quite different from that of substitutional diffusion.

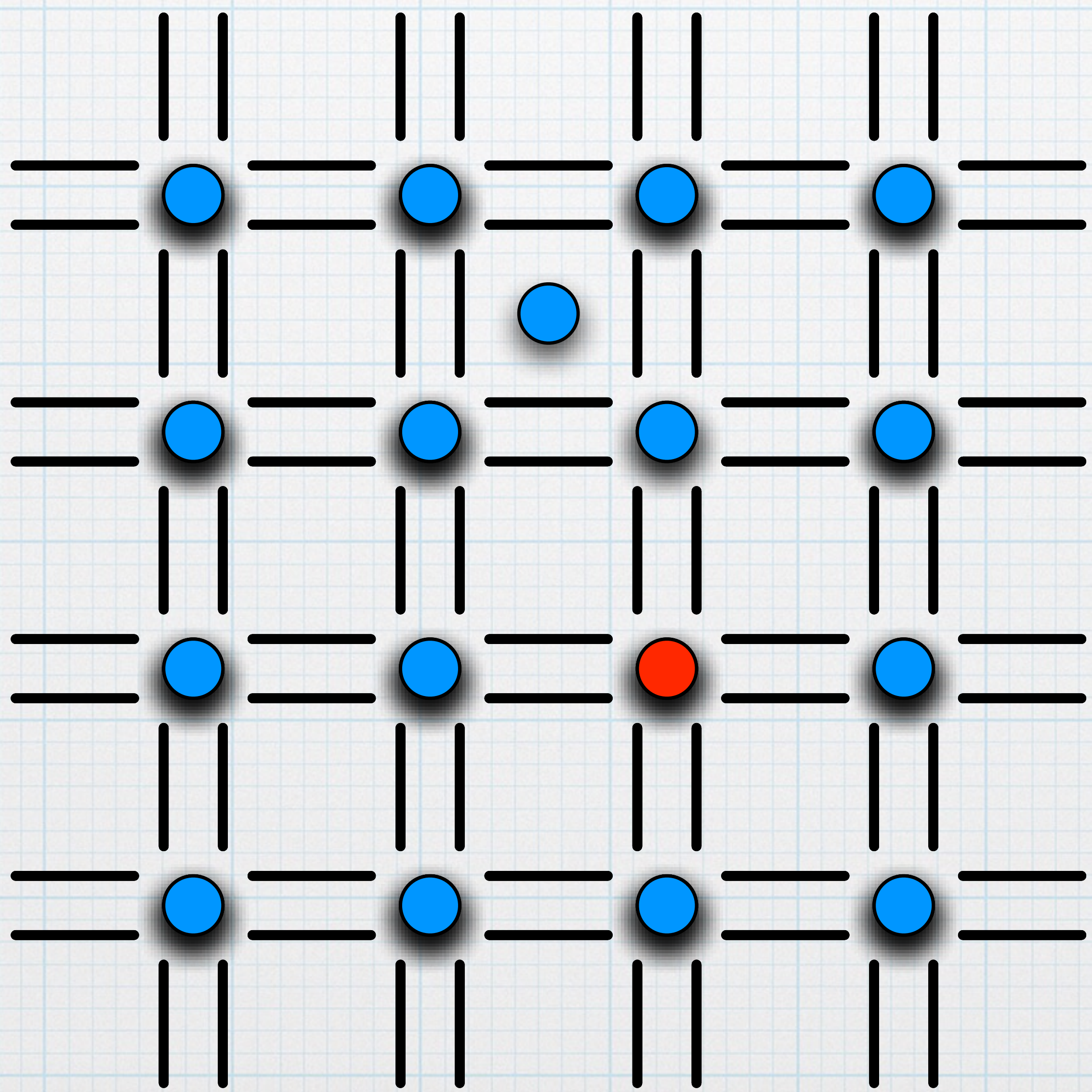


$$D_I = D_{OI} \exp\left(-\frac{E_{AI}}{k_B T}\right)$$

(Note that the impurity in the interstitial site is not electrically active.)

Some impurities may move only by substitutional diffusion, and some only by interstitial diffusion. Often there will be some aspects of both types of diffusion. So the "true" diffusion coefficient becomes a combination of the individual coefficients.

Point defects within the silicon lattice can have huge effect on diffusion coefficients. In particular, vacancies (missing silicon atoms) will enhance the diffusion rate.



The diffusion picture can become quite complicated, with impurities moving through substitutional sites, interstitial sites, interacting with vacancies, forming complexes (impurities and points defects moving together through the lattice), and more.

Although the diffusion equation is reasonably straight-forward as a macroscopic description of diffusion, the microscopic behavior, as given by the diffusion coefficient is much more complex, leading to concentration dependent diffusions and many examples of anomalous behavior.

One example is the “shoulder” that appears in phosphorus diffusion.