

3.044 Problem Set 8

Vapor Deposition Processes

Solutions

1. Mean free path and the Knudsen number

- One of the slides showed a transition to continuum behavior around a Knudsen number of 0.01, where the lengscale is the approximate size of the chamber.
- The uniformity of coverage of submicron patterned features using CVD depends on the ratio of mean free path to feature size, and the coating will be nonuniform (typically poor in the corners) if this ratio is large.
- Here the relevant Knudsen number is the ratio of mean free path calculated using vapor pressure λ_0 to source diameter. In the case of Problem Set 7 number 3d, we can estimate the total vapor pressure using the sum of vapor pressures times activities in the liquid $\sum \gamma_i X_i p_{vi}$:

$$X_{\text{Ti}} = \frac{\frac{0.81\text{g Ti/g total}}{47.88\text{g Ti/mol}}}{\frac{0.81\text{g Ti/g total}}{47.88\text{g Ti/mol}} + \frac{0.00123\text{g Al/g total}}{26.98\text{g Al/mol}} + \frac{0.19\text{g V/g total}}{50.91\text{g V/mol}}} = 0.817$$

$$X_{\text{Al}} = \frac{\frac{0.00123\text{g Al/g total}}{26.98\text{g Al/mol}}}{\frac{0.81\text{g Ti/g total}}{47.88\text{g Ti/mol}} + \frac{0.00123\text{g Al/g total}}{26.98\text{g Al/mol}} + \frac{0.19\text{g V/g total}}{50.91\text{g V/mol}}} = 0.002$$

$$X_{\text{V}} = \frac{\frac{0.19\text{g V/g total}}{50.91\text{g V/mol}}}{\frac{0.81\text{g Ti/g total}}{47.88\text{g Ti/mol}} + \frac{0.00123\text{g Al/g total}}{26.98\text{g Al/mol}} + \frac{0.19\text{g V/g total}}{50.91\text{g V/mol}}} = 0.181$$

$$p_v = (1 \cdot 0.817 \cdot 0.0123\text{torr} + 0.064 \cdot 0.06 \cdot 6.34\text{torr} + 1 \cdot 0.04 \cdot 0.0024\text{torr}) \frac{101300\text{Pa}}{760\text{torr}} = 1.52\text{Pa}.$$

This is quite close to the vapor pressure of pure titanium, so that would have worked as well. On to the mean free path and Knudsen number:

$$\lambda_0 = \frac{kT}{\sqrt{2}\pi\sigma^2 p_{v\text{Ti}}} = \frac{1.38 \times 10^{-23} \cdot 2023\text{K}}{\sqrt{2}\pi(7 \times 10^{-10}\text{m})^2 \cdot 1.52\text{Pa}} = 8.43\text{mm}.$$

$$\text{Kn} = \frac{\lambda_0}{d} = \frac{8.43\text{mm}}{25\text{mm}} = 0.337$$

You could either invert this and use the graph of n vs. Kn^{-1} , or use the equation from the paper

$$n = 1 + \frac{A}{B + \text{Kn}}$$

where $A = 0.0983$ and $B = 0.0321$, giving $n = 1.265$.

2. Structure zone model

- (a) To reduce the cosine power with the same total evaporation rate, one can use a larger source and a lower temperature.

Basically, in the graph of cosine power n vs. evaporation rate, turning up the beam power increased the source temperature, moving diagonally up along the curves at a given source size. This increased both evaporation rate and cosine power.

Now to get the cosine power back down at this new higher evaporation rate, we increase the source size to shift to a new curve to the right and slightly up, then decrease the temperature to shift down along that curve to reach the old n with the new higher total evaporation rate.

- (b) In the structure zone model, we've gone from equiaxed grains to faceted columnar grains, transitioning from zone 3 to zone 2.

To go back to zone 3, we can increase the substrate temperature.

- (c) Increasing the substrate temperature is likely to damage the fragile structures in the integrated circuit. So we might not be able to do that, and the whole effort to speed up the process might be fruitless.

On the other hand, it may be possible to speed up diffusion in a surface layer without increasing the temperature of the inside by bombarding it with an ion beam. With sufficient substrate cooling and just the right ion energy, one can heat up just the newly-deposited film and leave the deeper structures intact. It would be a pain to get this to work, and might not be worth the effort. Oh well.

3. Masking and patterning

- (a) In positive tone patterning, the radiative energy breaks bonds in the polymer, making it more soluble. The etchant then dissolves away the regions which have been exposed.

In negative tone patterning, radiative energy forms crosslinks between polymer chains, making the polymer less soluble. The etchant then dissolves away the regions which were *not* exposed.

- (b) Electron beam lithography can produce extremely fine features since the beam can be focused down to near the very small electron wavelength. For polymers whose cross-linking can be initiated by charge, this can also set off a chain reaction in which one cross-linking reaction charges the neighboring chain, initiating another cross-linking reaction, etc. The required energy per unit area is thus much smaller for certain polymers, such as the PGMA (poly(glycidyl methacrylate)) mentioned in class.

On the other hand, the beam must travel over a very complex path in order to "write" the patterns into the photoresist polymer, which can take a *very* long time for modern integrated circuits with large numbers of complex components; the required time thus scales roughly as the number of features. Far-UV lithography exposes the whole die or wafer at once, regardless of the complexity of the features.