Chromium oxide as a hard mask material better than metallic chromium

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In nanofabrication research, Cr is probably the most popular hard mask material for dry etching into silicon and its compound using fluorine-based gas. The Cr mask is typically patterned by lithography followed by either liftoff or direct dry plasma etch of Cr using the resist pattern as mask. For the latter case, it is critical to have a high etching rate selectivity between the resist and Cr, particularly for very high resolution pattern transfer for which the resist must be very thin, such as the case for sub-10 nm features formed by block copolymer lithography[1].

As standard photomask materials, respectively for light blocking and anti-reflection, the plasma etching of Cr and CrOx has been well established. Using Cl-containing gas (e.g. Cl_2 and CCl_4) and oxygen, the reactions are: $Cr+2O^*+2Cl^* \rightarrow CrO_2Cl_2$ (volatile at room temperature), $CrO_x+(2-x)O^*+2Cl^* \rightarrow CrO_2Cl_2$, here O* and Cl* are free radicals generated in the plasma[2,3]. Addition of oxygen to chlorine-based gas is essential, because otherwise the formed $CrCl_n$ (n=1-3) has very low vapor pressure (melting point of $CrCl_3$ is 1152 °C). Unfortunately, adding oxygen also considerably boosts the etching of the polymer resist, leading to a great reduction of etching selectivity between resist and Cr.

In this work we will show that CrO_x can achieve higher selectivity to resist than does Cr, and it is as efficient as Cr for masking the etching of silicon. Higher selectivity to resist for CrO_x was achieved because CrO_x contains oxygen by itself to promote fast etching even with low O_2 gas flow. This mechanism is somewhat similar to the etching of Si and SiO_2 using CHF_3 gas, which etches SiO_2 much faster than Si because the former contains oxygen to increase the F/C ratio (O reacts and consumes species like C in the plasma).

We used Oxford ICP-380 instrument for the etching of Cr and CrO_x that were deposited on silicon wafer by electron beam evaporation using respectively Cr and Cr_2O_3 source material, and we took polystyrene as an exemplary (negative) resist material that has an etching rate very close to that of ZEP-520A resist. It was found that the etching rates for both Cr and CrO_x were very low (<10 nm/min) if using only Cl_2 gas. By using the recipe below: 1200 W coil power, 10 W bias power, 12 mTorr, 50 °C, 80 sccm Cl_2, 8 sccm O_2, we obtained an etching rate of 37, 205, 56 nm/min respectively for polystyrene, CrO_x and Cr, showing nearly 4× faster etching of CrO_x than Cr. Importantly, as mask material for etching silicon using non-switching C_4F_8/SF_6 gas, the etching rate of CrO_x is nearly the same as that for metallic Cr. Therefore, it is evident that CrO_x is a better mask material than Cr. More systematic etching test and etching of Cr and CrO_x nanostructures to study e.g. the loading effect is under way and will be presented.

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