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Chromium oxide as a hard mask material better than metallic chromium

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In nanofabrication, use of thin resist is required to achieve very high resolution features. But thin resist makes pattern transferring by dry etching difficult because typical resist has poor resistance to plasma etching. One widely employed strategy is to use an intermediate hard mask layer, with the pattern first transferred into this layer, then into the substrate or sublayer. Cr is one of the most popular hard etching mask materials because of its high resistance to plasma etching. Cr etching is carried out in O2 and Cl2 or CCl4 environment to form the volatile etching product CrO2Cl2, but addition of O2 gas leads to fast resist etching. In this work, the authors show that Cr2O3 can be etched readily in a Cl2/O2 gas mixture with less oxygen than needed for Cr etching, because Cr2O3 contains oxygen by itself. Thus it is easier to transfer the resist pattern into Cr2O3 than into Cr. For the subsequent pattern transferring into the substrate here silicon using nonswitching pseudo-Bosch inductively coupled plasma-reactive ion etching with SF6/C4F8 gas and Cr or Cr2O3 as mask, it was found that the two materials have the same etching resistance and selectivity of 100:1 over silicon. Therefore, Cr2O3 is a more suitable hard mask material than Cr for pattern transferring using dry plasma etching. Published by the AVS. https://doi.org/10.1116/1.4998480

I. INTRODUCTION

Thin film plasma etching is one of the most important processes in semiconductor device fabrication for both industrial and R&D applications. Choice of the etching mask material is often as important as the etching recipe itself because it will determine the final structure’s morphology such as sidewall smoothness, taper angle, and feature resolution. Poor etching masks can cause rough or tapered sidewalls because of mask erosion.1 For a given etching selectivity between the mask and the material to be etched, higher etching depth requires thicker mask, but thicker mask structure is more difficult to fabricate with high resolution.2 Electron-beam resist and photoresists are apparently the most popular mask material. One of the well-known limitations for high resolution lithography using thick resist is pattern collapse caused by capillary force during rinsing liquid drying and after development. That is, in order to achieve very high resolution lithography, the polymer resist should be very thin such as 10–30 nm, leading to great challenge in pattern-transferring into the substrate because polymer resist usually has poor etching resistance.3 An apparent approach to greatly increase resist’s resistance to dry etching is to incorporate metal into organic polymer resists. One example is poly(sodium 4-styrenesulfonate), which is a water soluble and developable negative tone resist containing the metal sodium.4 A second example is organometallic metal carbonyl polymer, cyclopentadienylcarbonyldiphenylphosphinobutanoyliron, which contains metal iron.5 Alternatively, metal Cr can be incorporated physically into polystyrene (PS) resist using cothermal vaporization.6

A more popular approach to etch deep into the substrate is to use conventional polymer resist combined with an intermediate hard etching mask, where the intermediate hard mask is first patterned by lithography and pattern transferring, and then the substrate or sublayer is dry etched using the patterned hard mask structure as etching mask. Chromium (Cr) is probably the most widely utilized hard mask material for plasma etching because of its high selectivity to silicon and its compound when using fluorine or chlorine based etching chemistry. Use of Cr film was studied since 1976,7–10 and its applications include photomask as the opaque layer, etching mask in semiconductor device fabrication, and electrodes for thin film transistor liquid crystal displays and field emission displays (FEDs).11–14 Pattern transferring from the resist structure into Cr can be carried out either by lift-off or direct etching techniques using the resist as mask. Whereas lift-off is very popular for R&D because it patterns metals like Cr easily, it is rarely used by industry because of its low yield. In lift-off technique, the pattern edges are often not well defined, and metal flakes in the lift-off solution may stick onto other parts of the sample. In the direct etching pattern transferring method, wet etching or dry plasma etching can be performed, with dry plasma etching always preferred for high resolution nanofabrication. One disadvantage of the dry etching process is the usually poor etching selectivity between resist materials and metals. This is particularly true when Cr is used as the intermediate etching mask, because etching of Cr requires the addition of oxygen to the chlorine gas, and oxygen etches very fast the polymer resist material.

In this study, we will show that chromium oxide (Cr2O3) mask can achieve higher etching selectivity to resist than Cr does, and thus is easier to pattern by lithography followed by direct dry etching pattern transfer; and at the same time, for further pattern transferring into the substrate notably silicon, the patterned Cr2O3 is as efficient as metallic Cr as the intermediate hard mask material. Here, higher selectivity of
Cr_2O_3 to resist is obtained because Cr_2O_3 contains oxygen by itself that promotes the formation of the volatile etching product CrO_2Cl_2, and hence less oxygen is needed that in turn reduces the resist etching rate. Moreover, as it was discovered that Al_2O_3 is superior to Al as etching mask because it is insulating, we expect the same conclusion holds true for Cr_2O_3 as compared to Cr.

II. EXPERIMENT

In order to determine the etching rates of Cr and Cr_2O_3, over 300 nm thick of both materials were deposited on Si substrates using electron beam evaporator with Cr or Cr_2O_3 as source material. The film samples were then partially masked by a thick photoresist, and dry etching was carried out using Oxford 380 inductively coupled plasma-reactive ion etching (ICP-RIE) system. Afterward, the remaining resist was stripped away, and the resulted step heights were measured using a Veeco Dimension 3100 atomic force microscope. For etching Cr or Cr_2O_3, the chamber pressure, RF bias power, ICP coil power, total gas flow of Cl_2/O_2, and the chamber temperature were kept constant as 12 mTorr, 10 W, 1200 W, 50 sccm, and 50°C, respectively. While keeping the total gas flow at 50 sccm, the ratio between Cl_2 and O_2 was changed gradually to study the effect of O_2 percentage on the etching rate and selectivity for both materials.

To study the etching selectivity between Cr or its oxide and a polymer resist, we took PS as an example. Negative resist is preferred for this study, because it is more commonly used for pattern transferring by direct etching to fabricate protruded structures (to fabricate recessed structures by direct etching, positive resist is preferred). PS is a very versatile negative resist offering tunable sensitivity and contrast simply by varying its molecular weight. PS has a dry etching rate very close to that of ZEP-520A (positive) resist, and is two to three times slower than PMMA because PMMA is a linear polymer with higher oxygen content and higher radiation yield of chain scission reactions, whereas ZEP-520A has a stable phenyl group in its chemical structure. PS film of 400 nm thickness was coated on silicon wafer using spin coating method.

As standard photomask materials, respectively, for light blocking (Cr) and antireflection (Cr_2O_3), the plasma etching of Cr and Cr_2O_3 has been well established. Using Cl-containing gas (e.g., Cl_2 and CCl_4) and oxygen, the reactions are: Cr + 2O* + 2Cl* → CrO_2Cl_2 (boiling point 117°C, volatile at room temperature), and CrO_x + (2 - x)O* + 2Cl* → CrO_2Cl_2; here O* and Cl* are neutral free radicals generated in the plasma. Addition of oxygen to the chlorine-containing gas is essential, because otherwise the formed CrCl_n (n = 1 – 3) has very low vapor pressure at room temperature (melting point of CrCl_3 is 1152°C, and evaporation often does not maintain the chemical composition of the source material when depositing compound materials particularly alloys. This is caused by the different vapor pressures of each element in the compound at the evaporation temperature. It is therefore important to characterize the film composition of chromium oxide. As shown in Fig. 2, the energy-dispersive x-ray spectroscopy (EDX) measurement indicates that the evaporated film coated on a silicon substrate contains 60.4 at. % O and 39.6 at. % Cr, which is very close to the 3:2 atomic ratio in stoichiometric Cr_2O_3.

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III. RESULTS AND DISCUSSION

Unlike sputter deposition for which the film composition is always very close to the target material composition, evaporation often does not maintain the chemical composition of the source material when depositing compound materials particularly alloys. This is caused by the different vapor pressures of each element in the compound at the evaporation temperature. It is therefore important to characterize the film composition of chromium oxide. As shown in Fig. 2, the energy-dispersive x-ray spectroscopy (EDX) measurement indicates that the evaporated film coated on a silicon substrate contains 60.4 at. % O and 39.6 at. % Cr, which is very close to the 3:2 atomic ratio in stoichiometric Cr_2O_3.

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boiling/decomposition point $\sim$1300°C). Therefore, the amount of O\textsubscript{2} and Cl\textsubscript{2} or CCl\textsubscript{4} is important to determine the etching rate of Cr and Cr\textsubscript{2}O\textsubscript{3}. Unfortunately, adding oxygen also considerably boosts the etching of the polymer resist, leading to a great reduction of the etching selectivity between resist and Cr.

The etching rates with varying O\textsubscript{2} flow rates at a fixed total flow of Cl\textsubscript{2} + O\textsubscript{2} $\equiv$ 50 sccm for Cr, Cr\textsubscript{2}O\textsubscript{3} and PS are listed in Table I, as well as illustrated in Fig. 3 as a function of O\textsubscript{2} flow rate. As expected, decreasing O\textsubscript{2} flow from 8 to 3 sccm decreased the etching rate of PS from 45 to 31.5 nm/min, and the etching rate of Cr from 70 to 44 nm/min. However, the etching rate of Cr\textsubscript{2}O\textsubscript{3} was found to be constant at 130 nm/min. As a result, 10 nm PS resist would be enough to mask the etching of approximately 40 nm Cr\textsubscript{2}O\textsubscript{3} film using the 47/3 Cl\textsubscript{2}/O\textsubscript{2} gas flow ratio; whereas 10 nm PS can sustain the etching of only 17 nm Cr using the optimal 45/5 Cl\textsubscript{2}/O\textsubscript{2} gas flow ratio. This difference is caused by the fact that Cr\textsubscript{2}O\textsubscript{3} contains oxygen by itself to promote fast etching even with low O\textsubscript{2} gas flow. This mechanism is somewhat similar to the etching of Si and SiO\textsubscript{2} using CHF\textsubscript{3} or CF\textsubscript{4}/H\textsubscript{2} gas, which can etch SiO\textsubscript{2} much faster than Si because the former contains oxygen to increase the F/C ratio in the plasma (as O in the oxide reacts and helps remove species like CF\textsubscript{2},\textsubscript{3} and H to form volatile CO and H\textsubscript{2}O).

When only Cl\textsubscript{2} gas was used, the etching rate of Cr was found to be <1 nm/min, and that of Cr\textsubscript{2}O\textsubscript{3} was reduced to 11.3 nm/min. As the reduction in etching rate for PS is not as dramatic, the etching selectivity between Cr\textsubscript{2}O\textsubscript{3} and PS is lower. Therefore, addition of oxygen is essential and a gas flow ratio of Cl\textsubscript{2}/O\textsubscript{2} = 47/3 is considered optimal for our process.

It is equally important to have high etching selectivity between the hard mask material and the material to etch, here Si as an example. Therefore, etching rates of Cr\textsubscript{2}O\textsubscript{3}, Cr, and Si were examined using a nonswitching pseudo-Bosch process. It is found that the etching rate for Cr\textsubscript{2}O\textsubscript{3} was the same as that for Cr which was 4 nm/min, and the etching rate for Si was 390 nm/min that was nearly 100× faster than Cr.

<table>
<thead>
<tr>
<th>Gas flow of Cl\textsubscript{2} and O\textsubscript{2}</th>
<th>Material</th>
<th>Etch rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42 sccm Cl\textsubscript{2}, 8 sccm O\textsubscript{2}</td>
<td>Cr</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>45 sccm Cl\textsubscript{2}, 5 sccm O\textsubscript{2}</td>
<td>Cr</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>47 sccm Cl\textsubscript{2}, 3 sccm O\textsubscript{2}</td>
<td>Cr</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>50 sccm Cl\textsubscript{2}, 0 sccm O\textsubscript{2}</td>
<td>Cr</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PS</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

In this study, we reported that Cr\textsubscript{2}O\textsubscript{3} is a better choice than Cr as an intermediate hard etching mask material, where the resist pattern is first transferred into this material then into the substrate. This is because it contains oxygen by itself, and thus less oxygen is needed to be added to Cl\textsubscript{2} in order to form the volatile CrO\textsubscript{2}Cl\textsubscript{2} etching product. With less oxygen in the Cl\textsubscript{2}/O\textsubscript{2} gas mixture, the etching rate for resist, here polystyrene as an example of negative resist, is reduced, and hence it is easier to transfer the resist pattern into Cr\textsubscript{2}O\textsubscript{3} than into Cr. To achieve a high etching selectivity between Cr\textsubscript{2}O\textsubscript{3} and polystyrene resist, 47/3 Cl\textsubscript{2}/O\textsubscript{2} gas flow ratio has been found optimal with a selectivity of 4.1:1 (resist etches slower), as compared to the best selectivity of only 1.7:1 between Cr and polystyrene. For further pattern transferring into the substrate here silicon using nonswitching SF\textsubscript{6}/C\textsubscript{4}F\textsubscript{8} gas, it was found that Cr\textsubscript{2}O\textsubscript{3} has the same etching selectivity to silicon as Cr, both reaching a high value of 100:1.

![Fig. 3. (Color online) Etching rates of Cr, Cr\textsubscript{2}O\textsubscript{3}, and PS as a function of O\textsubscript{2} flow rate. Note that the etching condition and the etching rate values here are the same as those listed in Table I.](image)

![Fig. 4. SEM image of Si structures (Cr\textsubscript{2}O\textsubscript{3} mask still on) etched by non-switching pseudo-Bosch process.](image)
ACKNOWLEDGMENTS

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