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Lanthanum interaction with surface preparations

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Rare earth materials are used in different applications' fields such as optical, electric, magnetic and catalytic. They've been recently introduced in latest dies' generations with high k metal gate. When capped on this latter, they enable transistors' work function and devices' modulations. Various high k capping materials have been widely studied [1] [2]. Among these metals, lanthanum is of key interest. But, it also brings industrial challenges during its incorporation in an integration's scheme, hereafter described [3].

First of all, lanthanum film removability is considered. At pH lower than 7.5, La is very easily oxidized into La3+ (figure 1). Hence, acidic solutions and even deionized water quickly etch La away.

A deep chemicals' screening is performed to etch a 37Å plasma deposited lanthanum film. Conventional inorganic acids have been tested and give excellent La removal efficiency. Indeed HCl , and sulfuric acid are very efficient thanks to their strong acidity. Nonetheless, when HF and HCl are mixed together, lanthanum film isn't removed. This is probably due to a quick top surface passivation of the lanthanum film by LaF3, preventing this latter from being etched by HCl.

Less conventional chemicals have also been studied. Various chelating agents are tested, to bind La before it reacts with HF. Unfortunately glycolic acid generates exactly the same conclusion as HCl. More success is expected with stronger complexing agents.

Secondly, lanthanum removal is often combined with high k film removal. This latter operation usually requires the HF use. Therefore, one deals with La salts left on the wafer surface (figure 2). Even if they are tiny particles, their amount and affinity to be close to the transistors' gate can lead to unacceptable yield loss. Preventing La salts' deposition or enabling their removal is hence important.

Most of La salts have low solubility in water (figure 3 left) especially LaF3 (figure 3 left & right). Therefore wafer cleanliness has been checked during lanthanum removal operation. Whereas both glycolic and sulfuric acids remove completely the La film, this latter leaves numerous lanthanum sulfate salts (figure 4)

Finally, attempts to remove LaF3 salts on wafers will be conducted.

Conclusion

The use of rare earth materials in the integrated circuits' industry lead to new challenges. Lanthanum based films can be very quickly etched by many acids. But special care in selecting such acids is required to prevent salts precipitation due to low solubility of many Lanthanum salts in water. Managing correct use of HF in presence of Lanthanum on wafers has been hereby discussed.

References

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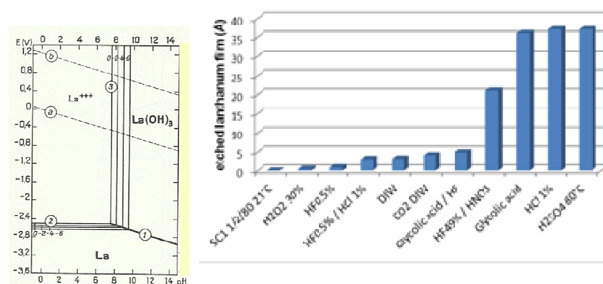


Fig 1. Pourbaix diagram of La in water (left)

37Å La film removal by various chemicals (right)

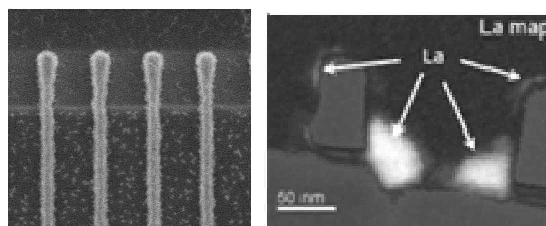
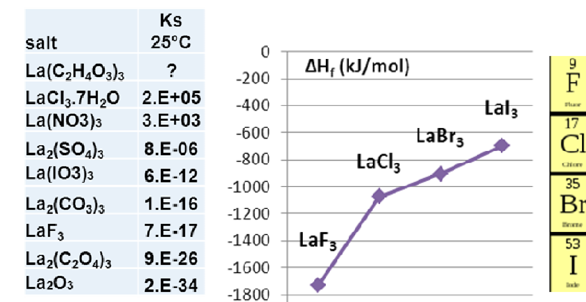


Fig 2. Lanthanum fluoride salts on product wafers



salt	Ks 25°C
$La(C_2H_4O_3)_3$	?
$LaCl_3.7H_2O$	2.E+05
$La(NO3)_3$	3.E+03
$La_2(SO_4)_3$	8.E-06
$La(IO3)_3$	6.E-12
$La_2(CO_3)_3$	1.E-16
LaF_3	7.E-17
$La_2(C_2O_4)_3$	9.E-26
La_2O_3	2.E-34

Fig 3 left solubility (left) & formation enthalpy (right) of various Lanthanum salts

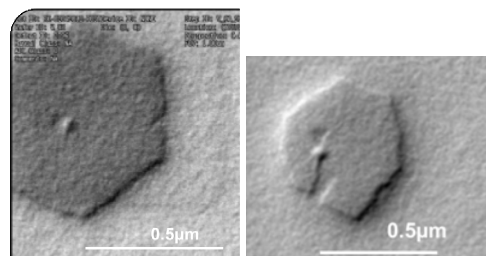


Fig 4: Lanthanum sulfate salts