

# Fluorocarbon Precursor for High Aspect Ratio Via Milling in Focused Ion Beam Modification of Integrated Circuits.

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## Abstract

Gas Assisted Etching (GAE) is the enabling technology for High Aspect Ratio (HAR) circuit access via milling in Focused Ion Beam (FIB) circuit modification. Metal interconnect layers of microelectronic Integrated Circuits (ICs) are separated by Inter-Layer Dielectric (ILD) materials, therefore HAR vias are typically milled in dielectrics.

Most of the etching precursor gases presently available for GAE of dielectrics on commercial FIB systems, such as  $\text{XeF}_2$ ,  $\text{Cl}_2$ , etc., are also effective etch enhancers for either Si, or/and some of the metals used in ICs. Therefore use of these precursors for via milling in dielectrics may lead to unwanted side effects, especially in a backside circuit edit approach. Making contacts to the polysilicon lines with traditional GAE precursors could also be difficult, if not impossible. Some of these precursors have a tendency to produce isotropic vias, especially in Si.

It has been proposed in the past to use fluorocarbon gases as precursors for the FIB milling of dielectrics. Preliminary experimental evaluation of Trifluoroacetic (Perfluoroacetic) Acid (TFA,  $\text{CF}_3\text{COOH}$ ) as a possible etching precursor for the HAR via milling in the application to FIB modification of ICs demonstrated that highly enhanced anisotropic milling of  $\text{SiO}_2$  in HAR vias is possible. A via with 9:1 aspect ratio was milled with accurate endpoint on Si and without apparent damage to the underlying Si substrate.

## Introduction

FIB GAE has been used extensively for the microelectronic circuit modification for almost two decades [1-3]. During these years, the range of GAE precursor gases utilized in industrial FIB systems for circuit modification applications has remained limited to  $\text{XeF}_2$  and halogens like  $\text{Cl}_2$ ,  $\text{I}_2$  and  $\text{Br}_2$  [4-6]. During the same period of time, the semiconductor industry went through a number of generations of IC technology, which involved significant reduction of feature size and thickness. Following these technological advances, circuit edit has evolved from the relatively simple “cut and paste” operation on one- or two-metal level circuitry [3] to an

extremely complex, multi-step process [6]. Modification of modern multi-layer microelectronic circuits requires extreme precision, and while the X/Y positioning and beam placement accuracy can be addressed by innovative system design, precision via depth control requires not only the enhanced endpoint sensitivity [7-8], but also improved material selectivity of the milling process. Improved selectivity is needed to ensure that FIB system and its operator are able to stop the milling process with minimal damage to the targeted conductor, while creating the circuit access via in the dielectric. To aid with this task, the ideal GAE precursor should enhance milling of dielectrics and inhibit milling of the conductors.

Etching enhancements of commonly used GAE precursors, available from references [4 – 6 and elsewhere], are summarized in *Table 1*. Reviewing the table, one can conclude that choosing the best GAE precursor for dielectric milling is not a trivial task, especially in the backside circuit edit application.

*Table 1: Etching yield enhancements of traditionally available FIB GAE precursors*

GAE Precursor	Si	$\text{SiO}_2$	W	Al
$\text{Cl}_2$	~ 8	~ 1	~ 1	8 ~ 16
$\text{Br}_2$	~ 6	~ 1	~ 1	6 ~ 10
$\text{I}_2$	~ 7	~ 1	~ 1	6 ~ 10
$\text{XeF}_2$	800 ~ 2800	7 ~ 10	8 ~ 10	~ 1

$\text{XeF}_2$  provides highest etch enhancement of the  $\text{SiO}_2$  dielectrics, but it is also a very aggressive enhancer of Si milling and known to attack Si spontaneously. When used for via access milling in backside circuit modification application, the  $\text{XeF}_2$  may cause damage to the active areas of circuitry due to spontaneous reaction with Si.  $\text{XeF}_2$  also enhances milling of W, and therefore it could be difficult to use  $\text{XeF}_2$  enhanced milling for contacting W plugs. Halogens do not attack Si spontaneously, do not enhance milling of W, and can be used to mill HAR vias in dielectric, albeit there is no dose enhancement and milling progresses much slower than with  $\text{XeF}_2$ . The halogens however enhance milling rate of Al and therefore endpoint detection for halogen-assisted HAR via

milling in dielectric on Al conductors may be difficult, if not impossible. HAR via milling endpoint detection on polysilicon line could be very difficult with either  $\text{XeF}_2$  or halogens, as Si etch enhancement is large in both cases and there is a risk to quickly mill through the thin poly line.

### Trifluoroacetic Acid as FIB GAE Precursor

A few fluorinated halocarbons, including Trifluoroacetic Acid (TFA) which is also known as “Perfluoroacetic Acid”, were proposed in the past [9] as precursors for FIB GAE of dielectrics. TFA is a chemical known for more than a hundred years; it is synthesized industrially and available in small and large quantities from a variety of chemistry suppliers. The physical properties of TFA, listed on the MSDS and available from the TFA manufacturers, make it suitable for delivery through common GAE apparatus: at room temperature the TFA is a thick, heavy liquid with boiling point close to  $72^\circ\text{C}$ , and a relatively high critical vapor pressure of 94 - 108 Torr. Therefore TFA can be relatively easily delivered into the high vacuum chamber of the FIB system by evaporation, either through the existing means, or through the recently proposed advanced gas delivery nozzle [10].

The exact mechanism of TFA-assisted GAE of dielectrics is not well understood, but it could be speculated that the mechanism is somewhat similar to the mechanism of  $\text{SiO}_2$  etching in fluoromethane plasma [11, 12]. As reported in [12], the  $\text{CF}_3^+$  ion provides the highest reactivity for  $\text{SiO}_2$  etching among the  $\text{CF}_x^+$ ,  $\text{C}^+$ , and  $\text{F}^+$  ions. Since the  $\text{CF}_3^+$  group is a major component of the TFA molecule  $\text{CF}_3\text{COOH}$ , the TFA is expected to provide a high etch enhancement of  $\text{SiO}_2$ -based dielectrics.

Qualitative explanation of the fluorocarbon assisted ion beam etching, proposed by the inventor of the process Dr. Clive Chandler [9], suggests that the reactive  $\text{CF}_3^+$  group of the fluorocarbon molecules is liberated during the ion beam induced reaction. The  $\text{CF}_3^+$  group is responsible for the  $\text{SiO}_2$  and other dielectric etching processes with the formation of volatile  $\text{SiF}_4$  byproduct, which is evacuated by the pumping system of the FIB. Oxygen atoms, contained in the molecules of  $\text{SiO}_2$  or other etched oxides, are released during the oxide etching process and believed to combine with the carbon atoms that are freed, as the fluorocarbon precursor reacts with the  $\text{SiO}_2$  or other oxygen-containing material.

If the etched material does not provide oxygen or other atoms to form a volatile compound with the carbon liberated during the etching process, the carbon will form a thin film on the surface of such materials and inhibit further etching enhancement. Therefore, etching of such materials as single crystal and polycrystalline silicon and metals should not be enhanced by the fluorocarbon precursors.

Results of preliminary experiments on TFA-assisted etching of  $\text{SiO}_2$  in a FIB system (**Fig. 1**) suggest that highly controlled TFA-enhanced etching of the dielectric is possible. Very precise endpoint on the Si substrate is also evident.

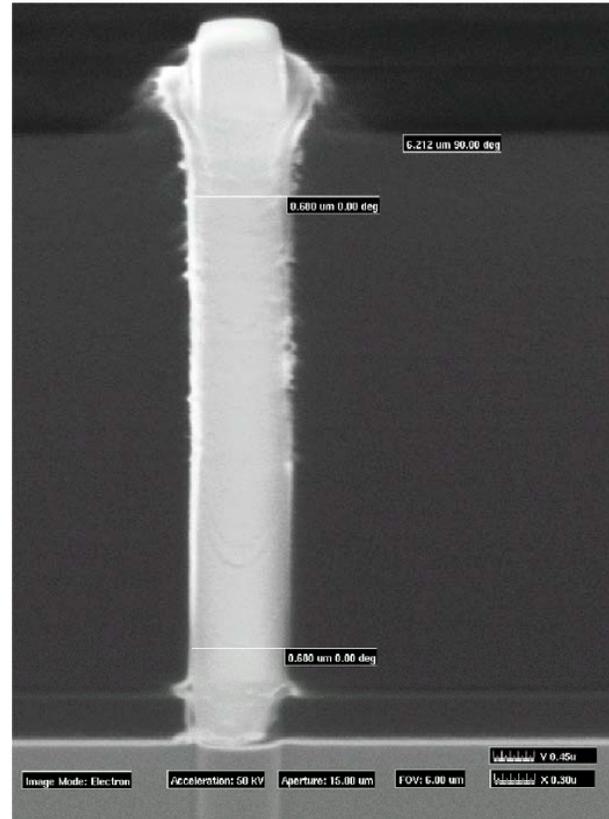


Figure 1: Cross-section of a HAR via milled by TFA-enhanced FIB GAE through  $\text{SiO}_2$  dielectric to Si substrate demonstrated good via profile control, precise endpoint and no damage to underlying Si.

### FIB GAE Recipe Development

While many FIB GAE recipes for milling of dielectrics were developed during the last two decades for  $\text{XeF}_2$  and halogen precursors, introduction of a new precursor with somewhat different properties could require additional process development effort. In contrast to the early days of FIB, sufficiently advanced FIB GAE theory is available today to provide guidelines and assist with the process development. It is worthwhile to review here the current state of the FIB GAE theory and discuss its application to practical recipe development in the HAR via milling application.

Since most of the modern FIB systems utilize some sort of digital raster generator to position the primary ion beam within the milling area, the discussion will be based on the digital scan model proposed by Harriott [13] and further developed by Edinger and Kraus [14, 15]. The model defines total yield of the substrate atoms that are removed by the FIB GAE process as:

$$Y = \frac{(\text{removed atoms})}{(\text{incident ions})} = \frac{(AR + AS)}{Jt_D}, \text{ where}$$

AR – number of the substrate atoms that have reacted with the precursor gas; AS – number of the substrate atoms removed by physical sputtering; J – flux of ions;  $t_D$  – pixel dwell time.

Thus the yield is defined as a number of the substrate atoms removed by incident ion. This relationship works very well either on surface of the sample or in shallow trenches, but it is easy to see that in the case of HAR via milling the relationship would not properly describe total yield of substrate atoms removed from within the via. As the mill is progressing into the substrate, the atoms removed by the physical sputtering will begin re-depositing on via sidewalls and overall yield of the substrate atoms from within the via will be reduced. One can also foresee the possibility, that in case of a very active precursor, large quantities of a physically sputtered material may cause damage to the via sidewalls by initiating a secondary GAE. In any case, physical sputtering of the material from the bottom of the via will slow via depth increase and lead to poor sidewall profile shape control. It becomes apparent from this discussion that a GAE recipe, suitable for milling of HAR vias, should be developed in such a way that removal of the substrate atoms will occur only (or primarily) by chemical mechanisms due to beam-initiated reaction of the substrate material with the precursor gas, and the physical sputtering should be minimized.

Published experimental results of yield dependence on the pixel dwell time [13-15 and elsewhere] indicate that the yield of the substrate material removal increases, as the pixel dwell time is reduced from about 5E-6 seconds to 2E-7 seconds. An explanation for this observation may be proposed by assuming that removing of the substrate material during the sufficiently long beam dwell within the single pixel location takes place in two separate phases which can be distinguished.

First, during a short period of  $t_{AR}$  in the beginning of the pixel dwell period, intensive chemical reaction of the substrate with the precursor gas adsorbed on the surface during the refresh time takes place. During the  $t_{AR}$  period of the beam dwell within the each pixel, material is removed primarily by the chemical reaction of the substrate with the precursor, quickly and with a large enhancement. Then, during the remaining  $t_{AS}$  fraction of the pixel dwell time, after the precursor has been depleted, material is removed primarily by a physical sputtering, combined with some chemical reaction with the precursor that is continuously adsorbed from the gas flux.

Thus  $t_D = t_{AR} + t_{AS}$  and it is apparent from the published experimental data that  $t_{AR} < 2E-7$  seconds. Therefore in order to achieve the highest possible enhancement, beam dwell within the pixel should be set as short as possible within the capabilities of the existing FIB tools.

Edinger and Krauss also demonstrated [15] that if distance between the overlapping pixels of GAE raster is increased, reducing the overlap, then the yield could be increased by as much as 20% - 50%. Therefore to achieve the highest yield possible, distance between the pixels of the GAE raster should be large enough for pixels to not overlap.

When the primary ion beam dwells at a certain pixel location, the precursor gas is depleted within the reaction area. Replenishment of the precursor gas is a relatively slow process and sufficient time should pass from the moment when the beam has left a certain pixel location within the raster until the moment when beam will complete the full raster and return to the same pixel. The period of time that is needed for precursor gas replenishment will depend on the type and local pressure of the precursor gas. Experimental results [13-21] suggest that refresh time  $t_R$  periods of 1 – 20 mSec are typical for the full replenishment of the precursor.

The GAE theory defines etching yield by the number of the substrate atoms per incident ion delivered by the primary beam, and therefore the theory can be applied directly to the development of GAE recipes aimed at achieving the highest possible dose enhancements. At the same time, it is not an unreasonable assumption that most users of industrial FIB systems would be interested in developing recipes that achieve not only the highest possible yield of substrate atoms per incident ion, but also the highest milling rate in terms of volume of substrate material removed per unit time. By utilizing the highest milling rate recipes, vias in circuit edit samples could be made in shortest time possible, thus maximizing productivity and utilization of the expensive FIB equipment.

A “first approximation” approach to the development of high milling rate GAE recipes could be to determine the optimal refresh time  $t_R$  for chosen precursor. Then, depending on the via size, the number of pixels within the via could be chosen in such a way that the full raster filled with pixels of a short dwell time  $t_D$  would take approximately the same time as the  $t_R$ :

$$N = t_R / t_D.$$

For the uniform square raster with the side dimension L distance between the pixels in X and Y directions would be

$$dX = dY = L / (\text{Sqrt}(N) - 1)$$

To avoid pixel overlap and consequent decrease in yield and the milling rate, the beam diameter, and consequently the beam current, could be chosen in such a way that the beam diameter will be equal to dX or little less than it.

The resulting GAE recipe would not only be optimized in terms of beam current as a function of the via size, but also will not include beam-blanking periods at the end of raster, thus minimizing the “beam idle time.” Fine-tuning of the

recipes by varying the parameters and employing statistical Design of Experiment (DOE) approaches and analysis software is possible. Further increase of milling rates could be achieved by advanced raster generation techniques, such as interlaced scanning and lissajous-like raster patterns, including raster patterns with non-uniform pixel distribution within the raster.

## Conclusions

Relatively obscure, but very promising fluorocarbon precursor for FIB GAE of dielectrics is demonstrated to be viable for HAR milling with good via profile control. Theoretical considerations for development of efficient FIB GAE recipes, based on the present state of the FIB GAE theory, are also introduced.

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