Invited talk

The long quest to understand etch mechanisms and surface science: The legacy of Harold Winters and its impact on semiconductor industry

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From the beginning of its days in semiconductor industry until now, Harold Winters work has very big impact to plasma processes and surface science. Starting with his landmark papers in the 1970's and 1980's, much scientific work was inspired by his publications. At IBM itself and industry-wide, many projects were impacted by his work. We will present our view on some of these topics as well as the lasting technological impact that Harold's work had and it inspired.

1 Some key discoveries of Harold Winters

One of the key drivers for miniaturization and reduction in overall cost has been the exploration of plasma technology for semiconductor applications. One of its pioneers, Harold Winters, helped tremendously with explaining its observed phenomena and diminishing the notion of a "black-box approach" [1]. His signature contribution to the field of plasma and surface science undoubtedly were the first demonstration of synergistic behavior of etch gas an ion bombardment.[2] Long before the advent of atomistic layer precision, Dr. Winters saw the need to study the surface science and unravel etch mechanisms exploring different etch chemistries. Most of his work focused on the etching of Silicon with XeF_2[3], however he also studied many other chemistries in order to understand the surface chemistries and understand the importance of certain reaction over others.[4,5] In his landmark paper on studying chemisorption in plasma etching [6], Winters found that the dissociative chemisorption does not influence the etching reactions, however that electron and/or ion bombardment will initiate reactions of the adsorbed species with the surface. He also commented on the extremely complex nature of the CF_x radical, which cannot be ignored when talking about etch mechanisms. Coburn and Winters then also introduced the concept of Fluorine to Carbon when discussing etch mechanisms for fluorocarbon processes.[7] Other significant contributions included the definition of physical and chemical sputtering mechanisms [8,9] and the early understanding that vacuum conductance arguments can be used to explain etch phenomena for high aspect ratio structures. [10] In addition, Harold Winters pioneered the study of surface science for plasma applications [11]. Harold Winters was also instrumental in providing cross section data for many gases, most notably CF_4 [12]. Last but not least, any new student in the plasma science field gets introduced to him by the quest for the prestigious AVS Coburn/Winters student award.

2 Impact of Winters work

The true impact of the work of Harold Winters is hard to be quantified. Due to his pioneering contributions on how to study surfaces during etch processes and formulate etch mechanisms, much of his impact is beyond measurable impact such as citations. We complied a selected subset of work, where H.F. Winters work was instrumental

2.1 Non-IBM work

Much of H.F. Winters legacy for plasma processing relies on the fact that he was able to explain much of the observed phenomena during a complex process such as plasma discharges and study it by using well controlled fluxes of species participating in the process. His decade long studies of photons, ions and radicals helped to unravel many mechanisms, and also proved to be a powerful tool to unravel damage mechanisms for new materials such as low-k. [13]

Based on his work on determining cross-sections of molecules such as CF_4, a large body of plasma discharge simulation was done. Maybe the most impactful study of this was the work by Edelson and Flamm. [14] Much of these theoretical and experimental studies of plasma discharges were an elemental part of the review by Flamm and Donnelly. [15] The biggest impact of Winters work was of course in the study of ion-enhanced etch mechanisms. Based on Winters work, Ninomiya [16], Steinbrüchel [17] and Vitale [18] studied the etch yield of materials and chemistries systematically and are landmark papers in this area themselves, which were consecutively further developed into dual linear relationships by J. Chang et al [19,20]. Winters' work continues to have big influence in new tool designs [21] or the study of novel materials. [22]

2.2 IBM work

Based on his initial work, many other IBM sites also continued to study phenomena based on Winters' publications. Seel and Bagus studied the interaction of fluorine and chlorine with Si (111) surfaces in detail.[23] N. Fuller and co-authors have presented work on low-k etch modification mechanism during resist removal in O_2, N_2 and H_2 containing discharges, which has received some critical reviews [24-26] The study of etch mechanisms for new materials in semiconductor manufacturing always draws from the foundational work of Winters to decompose complex processes and formulate etch models.[27,28] Last but not least, many of challenges faced in atomic layer etching (ALE) have its roots in the foundations laid by earlier Winters' publications [29,30] and are only beginning to be understood and developed further.

3 Legacy of Winters' work

As previously mentioned, the recent resurgence of ALE continues the legacy of Harold Winters' work. Even though Winters employed many novel methods to study surface chemistries, very little of these techniques have been applied to ALE approaches so far. In particular, the use of QCM [3] or flash filament and mass spectrometry [31] seem to be detrimental in unraveling etch mechanisms. In particular for new materials and new chemistries, the work by Harold Winters provides a fantastic framework by which new work in the field of ALE can be judged by.

Figure 1: Ion-assisted gas-surface chemistry using Ar^+ and XeF_2, on silicon. From [2]

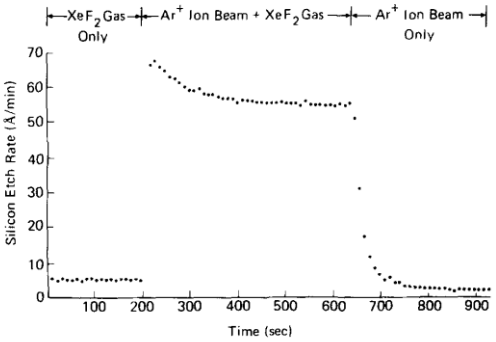
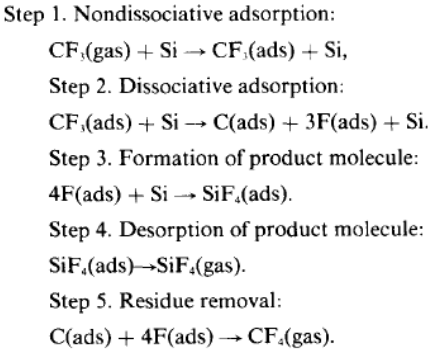


Fig. 2: Etching of solid material by exposure to gas-phase particles and proposed sequence of steps. From [3]


Step 1. Nondissociative adsorption:

$CF_4(gas) + Si \rightarrow CF_4(ads) + Si,$

Step 2. Dissociative adsorption:

$CF_4(ads) + Si \rightarrow C(ads) + 3F(ads) + Si.$

Step 3. Formation of product molecule:

$4F(ads) + Si \rightarrow SiF_4(ads).$

Step 4. Desorption of product molecule:

$SiF_4(ads) \rightarrow SiF_4(gas).$

Step 5. Residue removal:

$C(ads) + 4F(ads) \rightarrow CF_4(gas).$

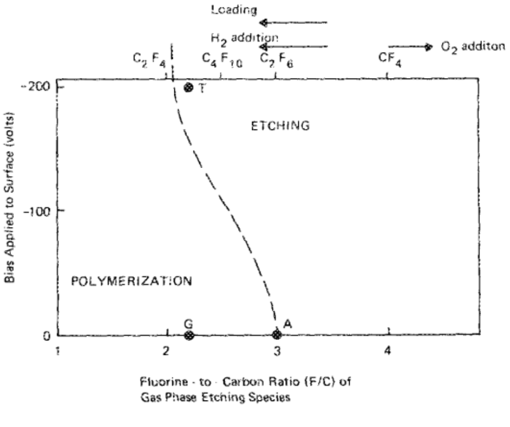


Fig. 3: Illustrative plot of the boundary between polymerizing and etching conditions as influenced by the fluorine-to-carbon ratio concept. From [7]

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