Fluorocarbon Plasma and Sustainable Replacements for Industrial Etching

Pingshan Luan

TEL Technology Center America, 255 Fuller Rd, Albany, NY, 12203

Abstract: Fluoride gases, including Fluorocarbon (FC) and hydrofluorocarbon (HFC), are essential chemical precursors for low temperature plasmas (LTPs) used in industrial etch processes. In this lecture, the chemistry of FC/HFC plasma will be reviewed, along with the mechanisms of their interaction with material surfaces. Sustainability of industrial processes involving FC/HFC plasmas will also be discussed.

1. Introduction

Fluorocarbon (FC) and hydrofluorocarbon (HFC) gases are the workhorse of industrial etching processes, essential for both logic and memory applications. When presented in low temperature plasmas (LTPs), FC and HFC precursors break down into neutral radicals and ions, which subsequently interact with surfaces to either subtract or add materials depending on plasma properties and surface compositions. Semiconductor etch processes exploit the complexity of FC/HFC plasmas-surface interaction to fabricate 3-dimensional structures at nanometer scale. Although being successful in the past 60 years, FC- and HFC-based processes face many challenges, particularly the environmental concerns and health impacts. In this lecture, we will review the fundamentals of FC/HFC plasma chemistry, their interaction mechanisms with material surfaces, and sustainable replacements for future applications.

2. Review of Conventional FC/HFC Etch Processes

The use of FC and HFC precursors in etching and cleaning applications grew with the rise of the semiconductor industry. Early researches focused on simple FC gases such as CF_4[1]. However, with the reduction of device size and the adoption of new materials, more sophisticated FC/HFC precursors, such as C_2F_6, C_3F_8, c-C_4F_8, C_4F_6, C_5F_8, CHF_3, CH_2F_2, CH_3F, *etc.* were gradually introduced. Non-carbon containing fluorides such as SF_6 and NF_3 are also offered as standard precursors on industrial etch chambers due to their ability of generating F-radicals in LTPs.

Though electron-impact dissociation and electron-impact ionization processes, various types of F- and C-containing neutral radicals and ions could be formed in the gas phase. Among these reactive species, CF_x neutrals and their low energy ionic counterpart are of particular importance for etch applications – they interact with surfaces and form fluorocarbon films. Such polymeric films are often deposited isotropically, with their thickness depends on not only the type of the precursors, but also material surface compositions and bias energy applied. By crafting the thickness and composition of these FC films, selective and/or directional etching of materials can be achieved. For example, in Figure 1, when Amorphous Carbon Layer (ACL) was used as mask, SiO_2 films can be patterned vertically with high aspect ratios.

3. Sustainable Alternatives

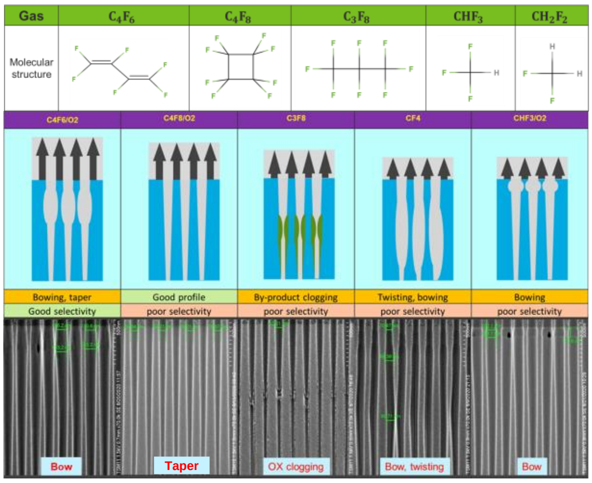

Fig. 1. Comparison of SiO_2 vertical etch profiles etched by various FC and HFC plasmas. Different FC and HFC precursors demonstrated drastically different etch defects, such as bow, taper, twisting, and clogging.[3]

Despite being indispensable for industrial etch processes, FC and HFC precursor are harmful to the environment in terms of both carbon footprint and toxic poly-fluorinated alkyl substances (PFASs) waste. The strong C–F bonds are stable which greatly extends the molecular lifetime of FC/HFC residues. Meanwhile the C–F bonds also absorb solar energy in spectral ranges 800 ~ 1600 cm^{-1} where the atmosphere is otherwise transparent.[2] In recent years, with the push towards a more sustainable semiconductor industry, cutting the use of FC/HFC gas becomes paramount. Faster etch processes, better abatement techniques, and new etchants with low molecular lifetime have all been adopted in the industry, and will remain important topics in the years to come.

Acknowledgement

The author thanks Dr. Peter L. G. Ventzek, Dr. Du Zhang, Dr. Yu-Hao Tsai, Mr. Sang-jin Chung, and Prof. Gottlieb S. Oehrlein for helpful discussions.

References

[1] J.W. Coburn., Journal of Applied Physics, 50, 5210-5213 (1979).
[2] G.S. Oehrlein, et al., JVST-B, 42, 4 (2024).
[3] P. Luan, GEC (2024)