Fragmentation of valence electronic states of C_3HF_5 studied by photoelectron photoion coincidence (PEPICO) techniques

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Abstract: C_3HF_5 is a promising, eco-friendly alternative to traditional perfluoro compound (PFC) gases for etching high-aspect-ratio dielectric stack (SiO_2/SiN) layers in advanced semiconductor manufacturing. This PEPICO study using synchrotron radiation provides valuable insights into fragmentation of valence electronic states of C_3HF_5.

1. Introduction

The semiconductor industry faces significant challenges in etching high-aspect-ratio (HAR) structures for fabrication of 3D flash memory. Traditional reactive ion etching (RIE) processes struggle with issues on aspect-ratio-dependent etching and require precise control to maintain high-quality profiles [1]. Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) gases are widely used in the HAR etching processes; despite their impact on global warming. To address these environmental concerns, the industry is exploring alternative gas chemistries and process techniques, including low-GWP fluorocarbons.

In this study, we have investigated dissociation of C_3HF_5 by the PEPICO technique using synchrotron radiation [2]. Identifying key dissociative fragments provided valuable insights for optimization of the etching results and minimization of their environmental impact.

2. Methods

C_3HF_5 (KSG-14, KANTO DENKA KOGYO., LTD) was used [3]. The PEPICO experiments were conducted at the UVSOR facility in Japan, utilizing a 2.5 m off-plane Eagle-type monochromator to generate tunable vacuum ultraviolet (VUV) light in the energy range of 10-26 eV. C_3HF_5 gas was introduced into a high-vacuum chamber and irradiated with the VUV light. A time-of-flight mass spectrometer was employed to detect the resulting fragment ions. By analyzing the ion yield curves as a function of photon energy, appearance energies were determined, providing valuable insights into the dissociation pathways and energetics of C_3HF_5 molecules.

3. Results and Discussion

Figure 1 presents the ion yield of C_3HF_5 as a function of photon energy, spanning from 10 to 26 eV, normalized to the photon flux of the VUV light source. A breakdown diagram was constructed from the ion yield curves, illustrating the relative ion abundance as a function of photon energy resulting from the dissociative ionization of C_3HF_5. Photoionization of C_3HF_5 yields predominantly $C_3HF_5^+$, $C_3F_5^+$, $C_3HF_4^+$, $C_3F_4^+$, $C_2F_3^+$, and CF_3^+ ions.

In the range of low photon energies 10.7-14.0 eV, $C_3HF_5^+$ ion dominates by photoionization of the parent molecule. $C_3F_5^+$ ion is produced by dissociative reactions $C_3HF_5 + hv \rightarrow C_3F_5^+ + H$.

As the photon energy increases, fragmentation pathways become more diverse, with $C_3HF_4^+$, $C_3F_4^+$, and $C_2F_3^+$ ions gaining prominence by the formation of counter fragments,

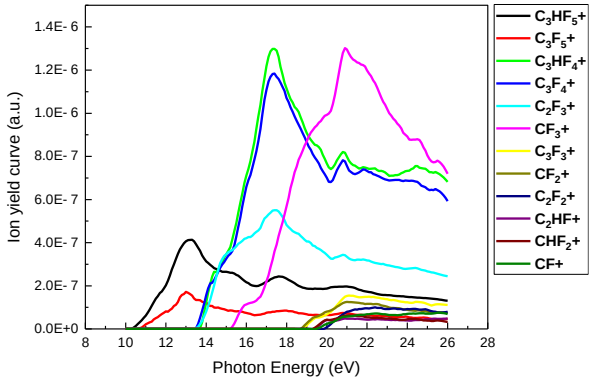

Fig. 1. Ion yield curves of the fragment ions produced from the photoionization of C_3HF_5.

F, HF, and HF_2, respectively. In the range of high energies 19-26 eV, CF_3^+ ion becomes increasingly abundant.

C_3HF_5 provides a rich source of reactive species $C_xH_yF_z^+$ ions, with forms such as $C_3HF_5^+$ and $C_3HF_4^+$, effective stoichiometric balance between H and F for etching SiN layers, while $C_xF_y^+$ ions, with forms such as $C_3F_4^+$ and CF_3^+, for etching SiO_2 layers in the HAR plasma etching.

4. Conclusion

The results obtained in this study provide valuable insights into the dissociation of C_3HF_5 and their potential role in etching of SiN and SiO_2 films. A deeper understanding of these fragmentations of HFCs can help optimization of selectivity control in plasma etching processes for improved HAR etching performance.

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