# Role of helium in plasma etching of silicon nitride by fluorine and hydrogen contained mixture


Yu. Barsukov[1], P. Pankratiev[1], A. Vinogradov[2], A. Kobelev[3], and A.S. Smirnov[1]

[1]*Department of Plasma Physics, Peter the Great Saint-Petersburg Polytechnic University, Saint-Petersburg, Russia*
[2]*Ioffe Physical-Technical Institue of Russian Academy of Science, Saint-Petersburg, Russia*
[3]*Center for Advanced Studies, Peter the Great Saint-Petersburg Polytechnic University, Saint-Petersburg, Russia*



**Abstract:** The fact that H-atoms enhance SiN etching in the presence of F-atoms was theoretically predicted. Here we present experimental data of SiN etching by $SF_6/H_2/He/Ar$ plasma. OES measurements for $H_2$/He and $SF_6$/He mixtures show that the He gas effects on $H_2$ plasma chemistry. Namely, addition of He in $SF_6/H_2$ mixture can selectively increase H-atom production in ground and excited states without changing of $SF_6$ dissociation degree. This feature of He can be used for SiN selective etching.



**Keywords:** plasma, etching, silicon nitride, helium, hydrogen, fluorine, $HeH^+$ ion.


## 1. Introduction

Plasma etching is widely used in semiconductor industry. Selective etching of silicon nitride (SiN) is an important issue in various applications used in integrated circuits manufacturing. The highly selective etching of SiN relative to silicon oxide and silicon is required in 3D-NAND flash memory manufacturing [1]. A remote plasma source can be used for isotropic selective etching of SiN in the horizontal direction between layers in the stack [2]. The SiN spacer is used for encapsulated of the ferroelectric materials during FRAM memory production. Anisotropic reactive-ion etching of SiN is required during the one of the steps of fabrication [3]. The detailed mechanism of enhanced SiN etching was proposed for NO reactant in our group previously [4]. It was theoretically predicted that H-atoms more effectively enhance SiN etching than NO reacting with fluorinated $SiNF_x$ surface [5]. Here we present experimental data about enhanced SiN etching by H-atoms in the present of F-atoms. It has been found that He effects on both Balmer lines intensities and SiN etch rate.

## 2. Experimental Setup

Direct capacitively coupled plasma etcher operating at 40 MHz was used in our experiments. SF6 (10.8 sccm) and $H_2$ (10 sccm) gases were chosen for production of F- and H-atoms in plasma discharge. Small amount of argon (1 sccm) was added in reaction mixture for actinometry measurements. The etcher is equipped with optical emission spectroscopy (OES) diagnostics. The 30 mTorr pressure and 300 W power were fixed, the flow rate of He was varied from 0 to 20 sccm.

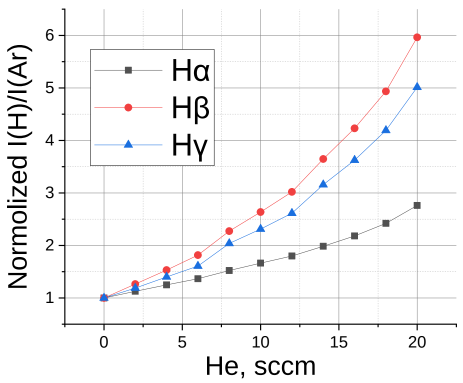


Fig. 1. Dependence of normalized Balmer lines on addition of He in $H_2$/Ar mixture.

## 3. Results

Balmer lines intensities have been measured. The normalized Balmer lines ($I(H_\alpha)/I(Ar)$, $I(H_\beta)/I(Ar)$, and $I(H_\gamma)/I(Ar)$ are presented in Fig.1. The normalized $H_\beta$ and $H_\gamma$ lines grow faster than $H_\alpha$ line. This can be explained by the fact of $HeH^+$ ion production. We assume that He in $H_2$ plasma generates $HeH^+$ ions at low pressure resulting in H-atoms in ground and excited states formation according to following mechanism:

He + H2+ → HeH+ + H (ground state) *(1)*

HeH+ + e → He + H* (n=5) *(2)*

HeH+ + e → He + H*(n=4) *(3)*

H*(n=5) → H*(n=2) + hv ($H_\gamma$ line) *(4)*

H*(n=4) → H*(n=2) + hv ($H_\beta$ line) *(5),*

where n is the main quantum number of H-atom. $HeH^+$ ion was detected in 1939 by M'Ewen and Arnot [6]. They suggested that the main channel of $HeH^+$ formation is reaction (1) with ~ 1.0 eV threshold energy number.

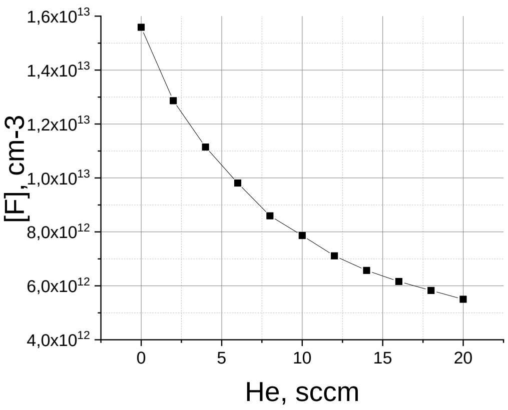


Fig. 2. Atomic fluorine concentration

We expect that $H_2^+$ should be in 4th vibrationally excited state to overcome the barrier (vibrational quantum of $H_2^+$ is 0.28 eV). The equilibrium H-H distance for $H_2^+$ ion is larger than for neutral molecule [7] therefore $H_2$ is ionized by electron impact in a vibrationally excited state due to Franck-Condon principle. It was shown in quantum chemistry calculations using full configuration interaction method that $HeH^+$ and HeH* (electronic excited states) have the bound states [8]. The potential curves for HeH* excited states which corresponds to He + H*(n=5) and He + H*(n=4) dissociation products lie close to $HeH^+$ curve at large H-He distance. Thus, we can assume that H*(n=5) and H*(n=4) are the more probable products of $HeH^+$ dissociative recombination then H*(n=3) and, as a result, $H_\beta$ and $H_\gamma$ grow faster than $H_\alpha$ (see reaction mechanism and Fig.1), which is excited only by electron impact. The different grow rates of Balmer lines have been observed for plasma discharges of both $H_2$/Ar and $SF_6$/$H_2$/Ar gas mixtures.

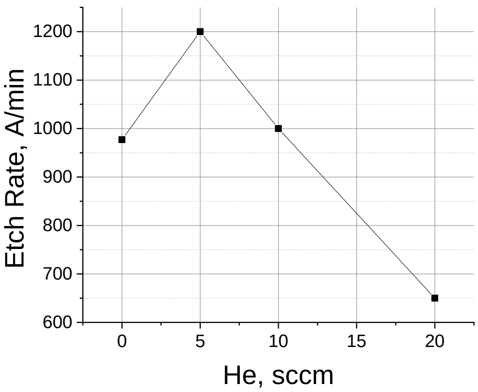


Fig. 3. Dependence SiN etch rate on He flow rate

The concentration of F-atoms has been measured using actinometry method and it was shown that helium does not change $SF_6$ dissociation degree (~1.5%) in plasma discharges of $SF_6$/Ar gas mixture and behaves like an inert carrier gas. The number of F-atom concentration has been obtained with the following expression:

$$[F] = C_{Ar}^{F}\ \frac{I(F)}{I(Ar)} n_{Ar}, \qquad (6)$$

where $C_{Ar}^{F}$ is actinometry coefficient (see Fig.2). It was shown in [9] that $C_{Ar}^{F}$ is constant in a wide range of plasma parameters and equals ≈2.0.

The etch rate of SiN has been measured for $SF_6$/$H_2$/Ar + He (0-20 sccm) mixtures. The SiN etch rate depends on He nonmonotonically and has a maximum value approximately at 5 sccm (see Fig. 3). This can be explained by the fact that initially etch rate growth due to H-atom production and then it drops because F-atom concentration decreases due to dilution.

## 4. Discussion

Analysing our experimental data, we assumed that addition of He in $H_2$ contained plasma strongly effects on plasma chemistry due to $HeH^+$ ion production. The main channel of $HeH^+$ formation is He + $H_2^+$ → $HeH^+$ + H reaction. Thus, He in $H_2$ contained plasma changes H-atom generation rate in the ground and excited states. On the other hand, $SF_6$ dissociation rate does not depend on He concentration. Thus, He can increase H-atoms production without changing the dissociation degree of other molecules. It should be note that high selective etching of SiN is possible at low concentration of F-atoms, because F-atoms etch all Si-based materials. Note, enhanced SiN etching is possible in the presence of F-atoms because F-atoms modify SiN surface into $SiNF_x$. On the next step N-atoms of modified $SiNF_x$ surface react with H or NO reactants. Thus, the reactants (NO or H-atoms) enhance etching of SiN only and, as a result, etch selectivity increases [4]. Selectivity is a very important issue of etching. Thus, this feature of He can be used for selective SiN plasma etching enhanced by H-atoms.

## 5. References


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