

Increase of cleaning rate and reduction in global warming effect during C_4F_8O/O_2 remote plasma cleaning of silicon nitride by adding NO and N_2O

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Abstract

During the chemical vapor deposition chamber cleaning and oxide etching processes using perfluorocompounds (PFCs), recombined and non-reacted PFCs are emitted. The emission of PFCs needs to be controlled in the near future to reduce the effect on global warming. In this study, an optimum condition of C_4F_8O/O_2 cleaning chemistry for silicon nitride by using a remote inductively coupled plasma source was determined as a function of process parameters. Under the optimum condition, the net emission of PFCs during cleaning was quantified using a Fourier transform-infrared spectroscopy and then the effects of additive nitrogen-containing NO and N_2O gases on the cleaning rate, the destruction removal efficiency and the million metric tons of carbon equivalent (MMTCE) were investigated. The addition of N_2O and NO gases to C_4F_8O/O_2 cleaning chemistry dramatically increased the cleaning rate by the factor of $\cong 9$ and decreased the volume of emitted CF_4 slightly. The increase in the cleaning rate and the decrease in the emitted volume of CF_4 by the addition of N_2O and NO contribute to the large decrease in the MMTCE values by 93 and 95%, respectively, compared to the case of cleaning without the additive gases.

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1. Introduction

Recently, the issue of the emission of global warming gases has become an important environmental concern worldwide. Perfluorocompounds (PFCs) emitted by the semiconductor industries are known to cause the global warming due to long atmospheric lifetimes and high global warming potentials (GWPs) caused by their strong absorption of infrared radiation. To prevent further increase of global warming by the emission of PFCs, the members of semiconductor industries have decided to reduce the emission level of PFCs responsible for global warming to 10% of the emission level of 1995 by 2010 [1].

Among the semiconductor fabrication processes, the direct plasma cleaning processes of silicon dioxide and silicon nitride in chemical vapor deposition (CVD) chamber using C_2F_6/O_2 are known to emit the largest

quantities of net PFCs. The reduction of emitted PFCs can be made by abating exhausted PFCs after processing or by replacing with alternative gases with less emission [2]. The use of alternative gases to the conventional C_2F_6 gas could be a fundamental solution. Direct plasma cleaning using various alternative gases such as C_3F_8 [3], C_4F_8 [4], and C_4F_8O [5] and remote plasma cleaning using NF_3 [6] having high destruction removal efficiency (DRE) have been studied to replace conventional cleaning process using PFCs such as CF_4 , SF_6 and C_2F_6 [5].

Recently, remote plasma cleaning process using NF_3 has been developed in order to minimize the erosion and damage of chamber parts during cleaning as well as to decrease global warming effect [6–8]. Remote plasma cleaning using NF_3/Ar chemistry, however, has some issues related to the cost of NF_3 gas and corrosion in the exhaust lines. Therefore, remote plasma cleaning process using less expensive gases such as C_4F_8 and C_4F_8O could be the best alternative solution due to

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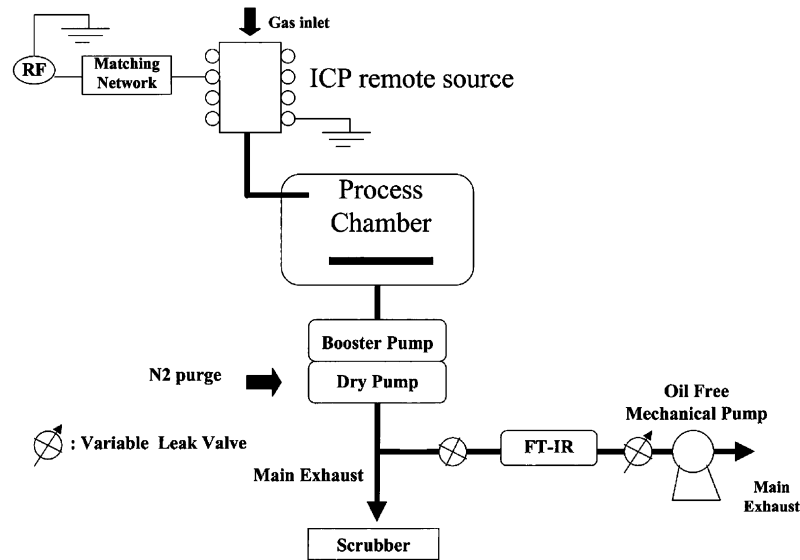


Fig. 1. Schematic of the remote plasma source and gas sampling system used for cleaning of the silicon nitride PECVD chamber.

lower cost and the advantage of remote plasma process. However, there have been no reports on the remote plasma cleaning process using alternative gases other than NF_3 .

In this work, cleaning processes of $\text{C}_4\text{F}_8\text{O}/\text{O}_2$ + additive gas using a remote inductively coupled plasma (ICP) source were investigated. Due to the limited cleaning rate of $\text{C}_4\text{F}_8\text{O}/\text{O}_2$ chemistry and higher million metric tons of carbon equivalents (MMTCE) values compared to NF_3/Ar chemistry, nitrogen-containing gases such as N_2O and NO were used as additive gases. Optimization of the cleaning process by adding N_2O and NO increased the cleaning rate by the factor of $\cong 9$ and $\cong 8.7$ and decreased the MMTCE by 93 and 95%, respectively, compared to those of $\text{C}_4\text{F}_8\text{O}/\text{O}_2$ cleaning chemistry.

2. Experiment

Fig. 1 shows a schematic diagram of the remote plasma source and the gas sampling systems used in this experiment for cleaning of the silicon nitride plasma enhanced chemical vapor deposition (PECVD) chamber. The remote plasma source was an ICP source operated at 13.56 MHz RF power. The water-cooled Cu tube was wound around the quartz tube and the mixture of cleaning gases was injected through the quartz tube. The Al chamber was evacuated using a pumping system combined with a booster pump and a dry pump to $\cong 1$ mTorr before the introduction of the mixture of cleaning gases. Square-shaped ($2 \times 2 \text{ cm}^2$) silicon nitride deposited on Si (001) was used as samples for cleaning experiment. The samples were located at the substrate holder, at the side wall, and at the front wall without heating and biased power.

Before measuring the emission of PFCs during cleaning of silicon nitride layers using $\text{C}_4\text{F}_8\text{O}$ feed gas, the flow rate of dilution N_2 for purging of dry pump and linearity of feed gas and targeted gas were checked by a Fourier transform-infrared spectroscopy (FT-IR; MIDAC, I2000). Dilution N_2 flow rate was 32 980 sccm in our experimental setup. This value was regularly checked to maintain the same experimental condition for every measurement. Slopes of concentration for feed gas and targeted gas flow rate diluted by N_2 ballast at dry pump was measured and used for calculation of the volume of emitted gases.

Silicon nitride samples were cleaned with the gas mixtures of $\text{C}_4\text{F}_8\text{O}/\text{O}_2$, $\text{C}_4\text{F}_8\text{O}/\text{O}_2 + \text{N}_2\text{O}$, and $\text{C}_4\text{F}_8\text{O}/\text{O}_2 + \text{NO}$, and the effects of additive N_2O and NO on the cleaning rate, DRE, and MMTCE were quantitatively evaluated. Cleaning rate of silicon nitride was measured using an α step-profilometer (Tencor, AS-500). The volumetric concentration of the species was measured by FT-IR. Optimum condition was obtained by controlling $\text{C}_4\text{F}_8\text{O}$ additive gas flow rate ratio, $\text{C}_4\text{F}_8\text{O}$ flow rate, and operational pressure. The applied RF power was kept constant at 800 W and working pressure at 400 mTorr.

Destruction of feed gas and the effect of emitted gases on global warming were quantified as DREs and MMTCEs, respectively. DRE and MMTCE values were calculated by using Eqs. (1) and (2), respectively

$$\text{DRE}(\%) = \left[1 - \frac{C_o}{C_i} \right] \times 100 \quad (1)$$

where C_i is the gas volumetric concentration before plasma cleaning and C_o is the gas volumetric concentra-

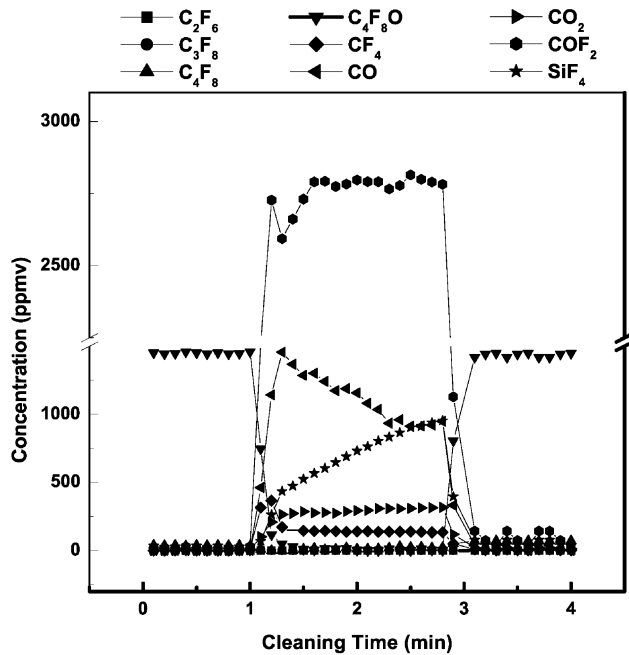


Fig. 2. Extractive FT-IR monitoring data during silicon nitride cleaning using C_4F_8O/O_2 chemistry.

tion after plasma cleaning, and

$$MMTCE = \sum_i \frac{12}{44} \times \frac{Q_i(\text{kg}) \times GWP_{100i}}{10^9} \quad (2)$$

where GWP_{100i} is the GWP of each component (integrated over a 100 year time horizon) and Q_i is the total mass of that species (in kg) released during the process [8]. Q_i can be calculated from the volumetric concentration data measured by FT-IR. Effects of the additive N_2O and NO gases on the MMTCE values were quantified based on the emitted volumes of PFC gases during cleaning of 1 μm -thick silicon nitride layer.

3. Results and discussion

Before the effects of addition of N_2O and NO gases are investigated, cleaning condition for C_4F_8O/O_2 chemistry was optimized by varying various process parameters such as working pressure, RF power of the remote source, flow rate, and total gas flow. The obtained optimum condition for C_4F_8O/O_2 cleaning chemistry used for the present experiments was the total gas flow of 220 sccm, the gas flow ratio of C_4F_8O (40 sccm)/ O_2 (180 sccm), the working pressure of 400 mTorr, and the RF power of 800 W. Under the above optimum condition, DRE and MMTCE values obtained from the quantitative measurement of the emitted gases by the FT-IR were 96% and 7.203×10^{-10} , respectively.

Fig. 2 shows the data of the FT-IR spectra obtained

under the optimized condition for C_4F_8O/O_2 cleaning chemistry. As seen from the Fig. 2, the main emitted species from the spectra are COF_2 , CO , SiF_4 , CF_4 and CO_2 . Most of the injected C_4F_8O molecules are dissociated and recombined into the other PFCs and F radicals react with the Si on the sample surface resulting in the generation of the by-products of cleaning process, SiF_4 . The volume of emitted COF_2 is quite large compared to the other gases but COF_2 was not included in the calculation of MMTCE because COF_2 can be removed easily by a wet scrubber [5]. Emission of NO and N_2O gases during cleaning was negligible. Among the emitted gases, therefore, C_4F_8 , CF_4 and CO_2 were included in the calculation of MMTCE.

There have been the experimental reports that the NO radicals formed in the remote plasma source can enhance the etch rate of silicon nitride layers by the increased surface reaction with nitrogen on the silicon nitride surfaces without the effect of ion bombardment on the surface [6,9–12]. Adding N-containing gases such as N_2 , NO and N_2O , therefore, may play a significant role in increasing the cleaning efficiency of CVD chamber. In order to investigate the effects of N-containing additive gases on the cleaning rate, DRE, and MMTCE values, N_2O and NO gases were added to the optimized C_4F_8O/O_2 chemistry.

Fig. 3 shows the cleaning rate and DRE values when 5–25% of N_2O gas was added to the optimized C_4F_8O/O_2 cleaning chemistry. At 15% of N_2O flow, the cleaning rate was greatly increased from 1180 $\text{\AA}/\text{min}$ without adding N_2O to 11 900 $\text{\AA}/\text{min}$, by the factor of $\cong 9$. Above 5% of N_2O flow, the cleaning rate of silicon nitride layers showed similar values. The DRE value $\cong 96\%$, was not changed significantly with adding N_2O

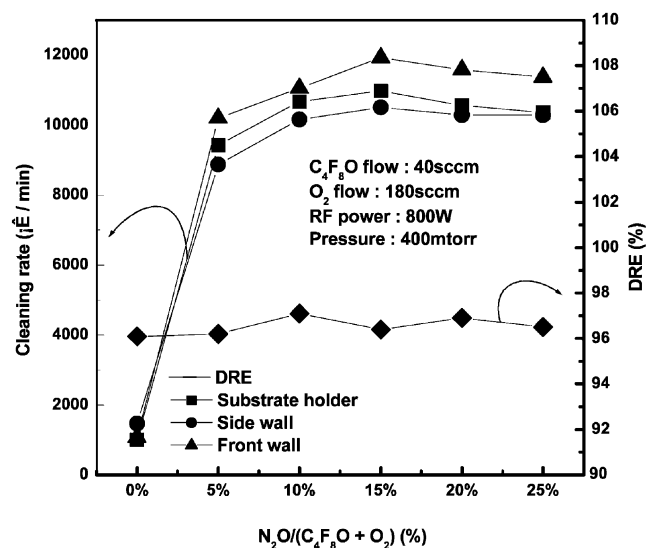


Fig. 3. The cleaning rate of silicon nitride at three positions and the DRE of C_4F_8O as a function of the percentage of N_2O to C_4F_8O/O_2 .

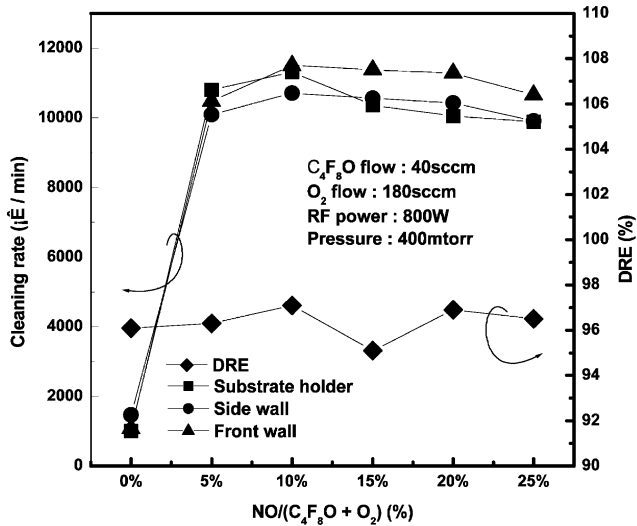


Fig. 4. The cleaning rate of silicon nitride at three positions and the DRE of C_4F_8O as a function of the percentage of NO to C_4F_8O/O_2 .

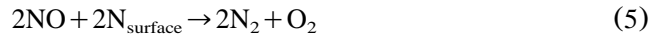
gas. The difference in the cleaning rate depending on the position of the samples was within 13%, which means uniform cleaning inside the chamber.

In order to investigate the effect of NO addition, NO gas was also added from 5 to 25% to the optimized C_4F_8O/O_2 cleaning chemistry. Fig. 4 shows the measured cleaning rate and DRE values. The cleaning rate was dramatically increased from 1180 Å/min without adding NO to 11 500 Å/min, by the factor of $\cong 8.7$, with adding NO above 5%. Similarly to the case of N_2O addition, DRE value $\cong 96\%$, was not affected significantly by the addition of NO gas. The difference in the cleaning rate depending on the sample positions is within 11%, which means the similar uniform cleaning inside the chamber to the case of N_2O addition. Observed uniform cleaning rate at different sample positions inside the chamber is attributed to the fact that the transport of the radicals participating in the cleaning is less dependent upon the chamber geometry and chamber pressure in the case of using a remote plasma source.

The observed dramatic increase in the cleaning rate with the addition of N_2O and NO is presumably attributed to the effective removal of nitrogen on the silicon nitride surface and in turn increased reaction of F radicals with Si-rich silicon nitride surface as discussed in the other Refs. [6,9–12]. Following the proposed model [6,9–12], in the example of N_2O , NO radicals can be formed by Eq. (3) although two Eqs. (3) and (4) are competitive and Eq. (4) is preferred [6,9–12].



Also, NO radicals can be generated by the reaction $N_2 + O \rightarrow NO + N$. Generated NO radicals can effectively react with N on the silicon nitride surface, N_{surface} , and make the surface Si-rich, by the following reactions:



Si-rich silicon nitride can be removed more effectively by the increased reaction rate of atomic F with silicon

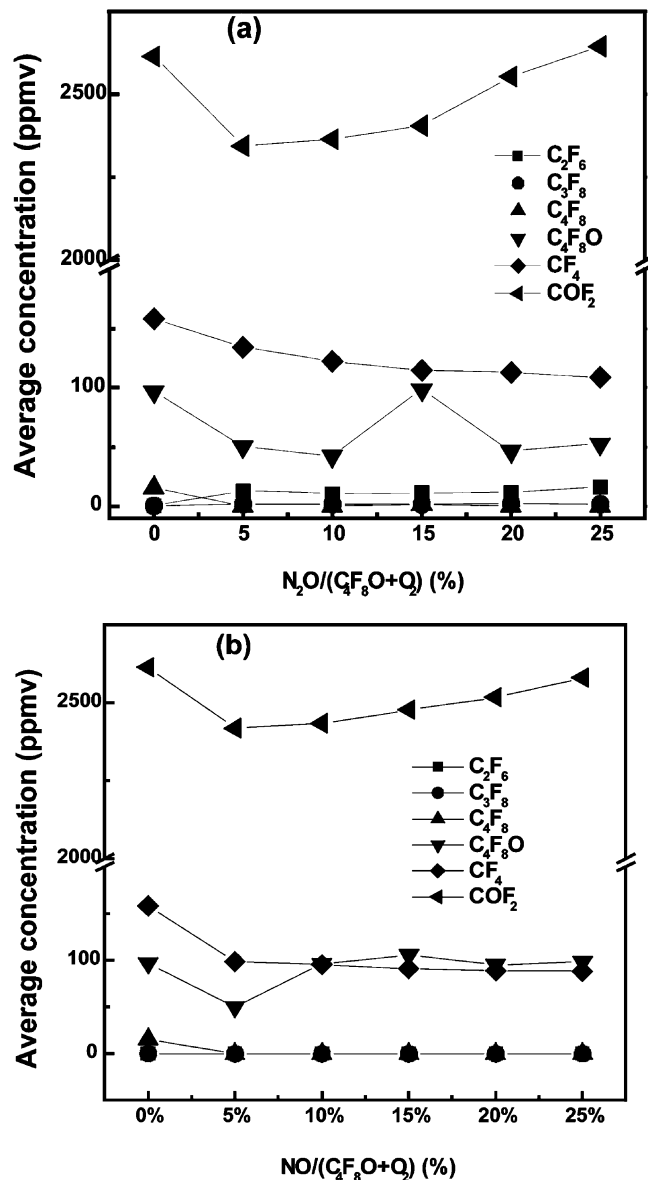


Fig. 5. The average concentrations of exhausted species as a function of the percentage of (a) N_2O and (b) NO to C_4F_8O/O_2 during the remote plasma cleaning.

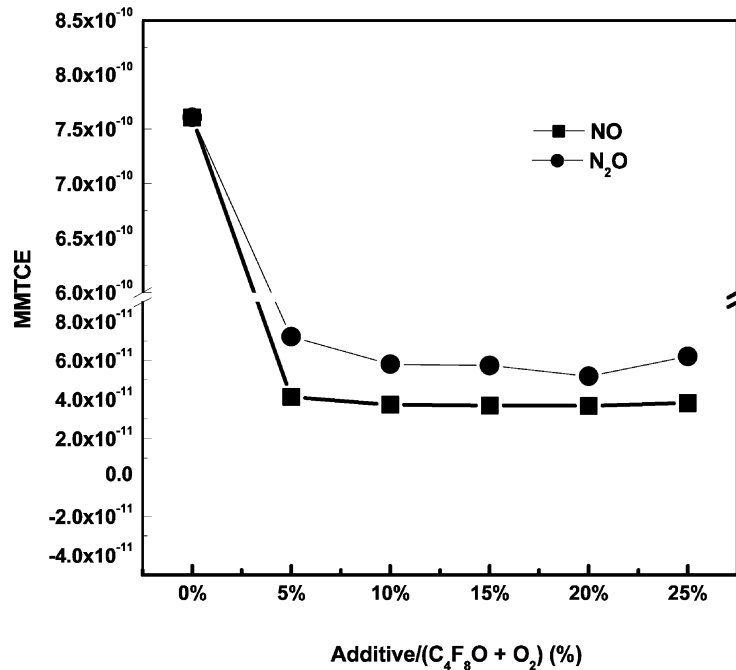


Fig. 6. MMTCE values during the silicon nitride cleaning as a function of the flow ratio of additive NO and N₂O.

atoms on the surface. Increased cleaning rate clearly contributes to the reduction in the usage gas during the cleaning of the same thickness of the silicon nitride layer, in the cleaning time, and in MMTCE.

In order to confirm the effect of additive N₂O and NO on the emission characteristics, the average concentrations of the emitted gases during cleaning are shown in Fig. 5a and b, respectively. As seen from the data in Fig. 5a and b, the average concentration of CF₄ with NO addition was slightly smaller than that with N₂O addition at the same percentage of additive gas. The more notable observation in the data in Fig. 5 is the decrease in the emitted amount of CF₄ with the addition of NO and N₂O gases. The decrease in the CF₄ emission also contributes to the decrease in the MMTCE values due to the significant emitted amount of CF₄ compared to other emitted PFCs.

Fig. 6 shows the MMTCE values obtained from Eq. (2) when N₂O and NO are added. When NO and N₂O above 5% are added above 5%, MMTCE values are dramatically decreased by 95 and 93% in average, respectively. The MMTCE values for the case of NO addition are slightly lower than those for the case of N₂O addition. This is attributed to the smaller emitted volume of CF₄ when NO was added than N₂O. The decrease in the MMTCE values with the addition of NO and N₂O is primarily caused by the increase in the cleaning rate together with the decrease in the amount of emitted CF₄. Therefore, adding N-containing additive gases such as N₂O and NO is very effective in increasing

the cleaning rate and, in turn, decreasing the MMTCE values.

4. Summary

The effect of N₂O and NO addition on the cleaning rate, DRE, and MMTCE values during the cleaning of silicon nitride was investigated in order to improve the cleaning performance of C₄F₈O/O₂ cleaning chemistry using a remote ICP source. The addition of N₂O and NO additive gases to C₄F₈O/O₂ cleaning chemistry dramatically increased the cleaning rate by the factor of $\cong 9$ probably due to the surface activated reaction of NO radicals formed from the remote plasma source with N on the silicon nitride surface leading to the increased reaction rate of F radicals with Si atoms on the surface. The increase in the cleaning rate and the decrease in the emitted amount of CF₄ by the addition of N₂O and NO contribute to the large decrease in the MMTCE values by 93 and 95%, respectively, compared to the case of the C₄F₈O/O₂ without the additive gases. These results indicate the effectiveness of the addition of N-containing to PFC-based chemistry for the environmentally-benign chamber cleaning process in semiconductor industry

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References

- [1] International Technology Roadmap for Semiconductors, 248 (1999).
- [2] W.T. Tsai, H.H. Chen, W.Y. Hsien, J. Loss Prevent. Proc. 15 (2002) 65–75.
- [3] L. Zazzera, S. Kesari, W. Reagen, L. Tousignant, W. Holber, X. Chen, Electrochemical Society Proceedings (1999) 99-8, 10-19.
- [4] M.T. Mocella, ISESH Eighth Conference (2001) 18–20.
- [5] L. Pruette, S. Karecki, R. Reif, L. Tousignant, W. Reagan, S. Kesari, L. Zazzera, J. Electrochem. Soc. 147 (3) (2000) 1149.
- [6] B.E.E. Kastenmeier, P.J. Matsuo, G.S. Oehrlein, J. Vac. Sci. Technol. A 16 (4) (1998) 2047.
- [7] P.J. Matsuo, B.E.E. Kastenmeier, J.J. Beulens, G.S. Oehrlein, J. Vac. Sci. Technol. A 15 (4) (1997) 1801.
- [8] S. Raoux, T. Tanaka, M. Bhan, H. Ponnkanti, M. Seamons, T. Deacon, L.-Q. Xia, F. Pham, D. Silveti, D. Cheung, K. Fairbairn, J. Vac. Sci. Technol. B 17 (2) (1999) 477.
- [9] J.J. Beulens, B.E.E. Kastenmeier, P.J. Matsuo, G.S. Oehrlein, Appl. Phys. Lett. 66 (20) (1995) 2634.
- [10] M.G. Blain, T.L. Meisenheimer, J.E. Stevens, J. Vac. Sci. Technol. A 14 (4) (1996) 2151.
- [11] B.E.E. Kastenmeier, P.J. Matsuo, J.J. Beulens, G.S. Oehrlein, J. Vac. Sci. Technol. A 14 (5) (1996) 2802.
- [12] B.E.E. Kastenmeier, P.J. Matsuo, G.S. Oehrlein, R.E. Ellefson, L.C. Frees, J. Vac. Sci. Technol. A 19 (1) (2001) 25.