

# Selective reactive ion etching of silicon nitride over silicon using CHF<sub>3</sub> with N<sub>2</sub> addition

Y. X. Li, P. J. French, and R. F. Wolffenbuttel

Laboratory for Electronic Instrumentation, Department of Electrical Engineering, Delft University of Technology, Mekelweg 4, 2628 CD Delft, The Netherlands

(Received 3 January 1995; accepted 7 July 1995)

In this article the effects of process parameters of CHF<sub>3</sub>+N<sub>2</sub> plasma etching chemistry (rf power 50–70 W, pressure 22.5–52.5 mTorr, and N<sub>2</sub> content 0%–95%) and mask materials (photoresist, aluminum, and silicon nitride) on the etching selectivity of silicon nitride over polysilicon are investigated. It was found that the selectivity increased with the N<sub>2</sub> content in the range of 0%–85% and then decreased, leading to the maximum selectivity (16) at 7.5 sccm CHF<sub>3</sub>+42.5 sccm N<sub>2</sub> (85% N<sub>2</sub>) at 60 W and 37.5 mTorr. The selectivity increased linearly with power and decreased with pressure. The higher the Si/N ratio of the nitride, the faster the nitride is etched. No influence of the residual stress level on the etch rate of the nitride was observed. The selectivity with resist masks was found to be higher than with either aluminum or nitride masks. Removal of N atoms is suggested to be one of the major rate-limiting factors in the nitride etching. It is argued that the addition of N<sub>2</sub> in CHF<sub>3</sub> dilutes the polymer-forming radicals and generates abundant N atoms, which diffuse to the substrate and combine with the N atoms adsorbed there due to etching. Both of these effects enhance nitride etch rate. © 1995 American Vacuum Society.

## I. INTRODUCTION

Silicon nitride is widely used in microelectronics as a dielectric, masking layer in localized oxidation of silicon (LOCOS) processes and passivation layer in silicon integrated circuit technology. It plays an important role in the fabrication of silicon-based sensors and actuators due to its superior mechanical properties. For example, it is used as the mask for KOH etching in bulk micromachining,<sup>1</sup> the rotor for micromotors,<sup>2</sup> or the membrane for micromachined tactile sensors<sup>3</sup> in surface micromachining. Conventionally, silicon nitride can be patterned using wet chemicals such as hot phosphoric acid. However, wet etching methods result in isotropic etching profile, which make it very difficult to achieve feature sizes less than 3 μm. Therefore, plasma etching is used almost exclusively in the modern microelectronic fabrication technology owing to its etching anisotropy. This anisotropy results from the ion bombardment of the substrate surface during etching, which enhances the etching in the vertical direction. However, the substrate underneath the nitride (silicon or silicon dioxide) may also be etched during plasma etching. This is because the reactants (gases) usually used in the nitride plasma etching also etch silicon and silicon dioxide. As a result, selectivity is one of the issues of major concern in the etching gas selection. To obtain a high selectivity over silicon, a chemistry such as CHF<sub>3</sub> (Refs. 4–6) or CF<sub>4</sub>/H<sub>2</sub> (Ref. 7) is generally chosen, which contains both reactive species such as F atoms and CF<sub>x</sub><sup>+</sup> (x=1–3) ions and polymer-forming precursors such as CF<sub>y</sub> (y=1–3) radicals. The reactive species etch nitride with the help of energetic ion bombardment, while the CF<sub>y</sub> radicals form a C–F polymer layer on the silicon substrate, which retards the etching of the substrate by the reactive species. Many gas mixtures providing such etching characteristics have been used in selective etching of nitride over silicon, including CHF<sub>3</sub>+O<sub>2</sub>,<sup>4</sup> CHF<sub>3</sub>+CO<sub>2</sub>,<sup>4</sup> CHF<sub>3</sub>+CH<sub>4</sub>,<sup>8</sup> CF<sub>4</sub>+CH<sub>4</sub>,<sup>8</sup>

CF<sub>4</sub>+H<sub>2</sub>+He,<sup>9</sup> and SiF<sub>4</sub>+O<sub>2</sub>.<sup>10</sup> With these gases selectivities of 10–12 have been achieved. Using a downstream plasma etcher with SF<sub>6</sub>+H<sub>2</sub>+He,<sup>9</sup> a selectivity as high as 40 has been reported. However, in this reactor etching is isotropic because the downstream configuration results in pure chemical reactions only. Using feed gases with high C/F ratio such as C<sub>2</sub>F<sub>6</sub>,<sup>11</sup> C<sub>2</sub>F<sub>6</sub>+C<sub>2</sub>H<sub>4</sub>,<sup>12</sup> cyclo-C<sub>4</sub>F<sub>8</sub>,<sup>12</sup> and C<sub>3</sub>F<sub>8</sub>,<sup>13</sup> selectivities of 10–20 have been reported.

It has been pointed out that molecular nitrogen is the major nitrogen-containing reaction product of silicon nitride etching. However, the distance between the adjacent nitrogen atoms in Si<sub>3</sub>N<sub>4</sub> (~2.8 Å) is larger than a N–N single bond distance (~1.5 Å). Thus adjacent nitrogen atoms, in a silicon depleted Si<sub>3</sub>N<sub>4</sub> structure, are not in sufficiently close proximity to form a bond. For N<sub>2</sub> to form at the surface it is necessary that reorganization of the surface structure takes place subsequent to F atom attack.<sup>14</sup> In other words, desorption of nitrogen atoms on Si<sub>3</sub>N<sub>4</sub> surface is one of the main factors which limit the etch rate. If additional nitrogen atoms are introduced in the system it is expected that these may combine with the nitrogen atoms attached to the surface by abstraction reactions, thus enhancing the nitride etching.

In this article a plasma etching chemistry using CHF<sub>3</sub> with N<sub>2</sub> addition for selective etching of silicon nitride over polysilicon is described. It is shown that the etch rate of the nitride and selectivity over polysilicon increase with the N<sub>2</sub> content, leading to a maximum selectivity of 16.

## II. EXPERIMENTS

The plasma etching was performed in a commercial parallel-plate reactive ion etching (RIE) machine (Alcatel GIR300). The rf power (frequency 13.56 MHz) and gas pressure were varied from 50–70 W and 22.5–52.5 mTorr (0.03–0.07 mbar), respectively. Both the upper and lower electrodes were 15 cm in diameter with a 6.5 cm spacing,

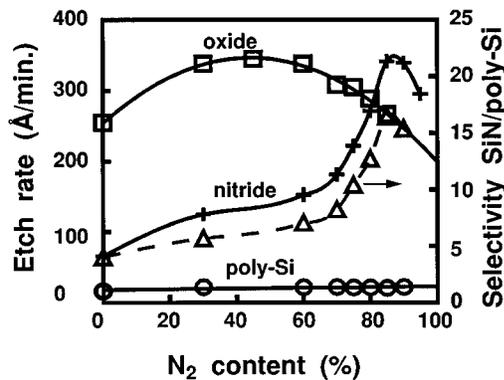


FIG. 1. Etch rates of polysilicon, silicon nitride and oxide, and selectivity of nitride over polysilicon vs  $N_2$  content in the  $CHF_3+N_2$  chemistry. rf power=60 W, pressure=37.5 mTorr, the total flow rate=50 sccm.

resulting in a corresponding power density of 43–62  $mW/cm^2$ . The total gas flow rate of  $CHF_3+N_2$  was 50 sccm. Helium gas was also used instead of  $N_2$  to dilute  $CHF_3$  gas. A 1.3  $\mu m$  HPR 204 photoresist was used as the mask for etching. For comparison, 0.6  $\mu m$  Al or 0.3  $\mu m$  silicon nitride was also used as the etch mask to examine the influence of the mask materials.

The silicon nitride used in the experiment was deposited on a (100)  $p$ -type 5  $\Omega cm$  silicon substrate using a low-pressure chemical vapor deposition (LPCVD) system (Tempress Omega M) operating at 850  $^\circ C$  and 150 mTorr. The reaction takes place between  $SiH_2Cl_2$  (170 sccm) and  $NH_3$  (30 sccm) in a 15-cm-diam quartz tube to form silicon nitride which is silicon rich (Si/N ratio of 0.82) and exhibits low tensile stress.<sup>15</sup> The polysilicon film under the nitride was formed also in a similar LPCVD system in which silane decomposition takes place at 575  $^\circ C$  and 150 mTorr. Polysilicon films of 3000  $\text{Å}$  were doped by phosphorus implantation of  $5 \times 10^{15} cm^{-2}$  at 80 keV and subsequently thermally annealed at 850  $^\circ C$  for 30 min in  $N_2$  atmosphere, yielding a sheet resistance of about 200  $\Omega/\square$ . The silicon dioxide films used were formed by oxidation in dry oxygen at 1100  $^\circ C$ .

The etch rate of the films was determined by measuring the thickness change due to etching using a Leitz MPV-SP optical measurement system.

### III. RESULTS

#### A. The effects of $N_2$ content in $CHF_3+N_2$ gas mixtures

Figure 1 shows the dependence of etch rate of the silicon nitride, silicon dioxide, and polysilicon and the selectivity of nitride over polysilicon on  $N_2$  content in the gas mixtures of  $CHF_3+N_2$ . The power, pressure, and total gas flow rate were fixed at 60 W, 37.5 mTorr, and 50 sccm, respectively. Note that without  $N_2$ , a pure  $CHF_3$  chemistry etches the nitride with an etch rate of 70  $\text{Å}/min$  and a selectivity of 4 over the polysilicon. The etch rate for the nitride increases dramatically with the  $N_2$  content in the range of 0%–85% and starts to drop when the content is further increased to 95%. However, no change of the etch rate of the polysilicon could be measured in the  $N_2$  content range of 0%–95%. Therefore, the

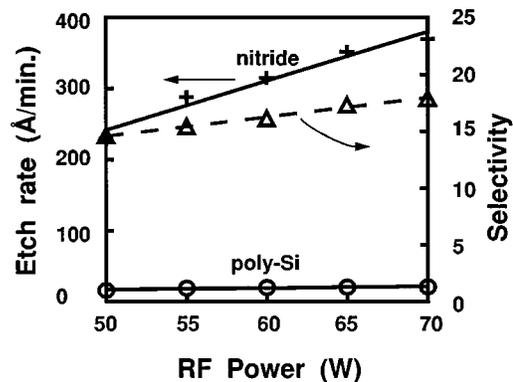


FIG. 2. Effects of rf power on the etch rates of nitride and polysilicon and the selectivity. Pressure=37.5 mTorr,  $CHF_3=7.5$  sccm,  $N_2=42.5$  sccm.

selectivity increases with  $N_2$  content in the 0%–85% range, which reaches its maximum of 16 at 85% (42.5 sccm)  $N_2$ . This gas composition (7.5 sccm  $CHF_3+42.5$  sccm  $N_2$ ) was further used in the remaining experiments concerning rf power, gas pressure, mask materials, nitride composition, and residual stress in nitride. At an  $N_2$  content above 95%, the plasma cannot be ignited due to the limited range of adjustment of the automatic network matching system. The etch rate for the oxide varies with the  $N_2$  content in the similar way as that for the nitride. However, the oxide etch rate without  $N_2$  addition is higher and reaches its maximum at lower  $N_2$  content (45%) compared to the nitride etch rate.

#### B. The effects of rf power and gas pressure

Figures 2 and 3 show the etch rates of the nitride and polysilicon and the selectivity versus rf power and gas pressure, respectively. The pressure used in the experiment for Fig. 2 is 37.5 mTorr and the power in Fig. 3 is 60 W. Clearly the etch rate for the nitride increases with the power, while that for the polysilicon remains essentially unchanged. This etch rate dependence on the power results in the increase of the selectivity with the power, as indicated in Fig. 2. Figure 3 shows that the etch rate of the nitride decreases with

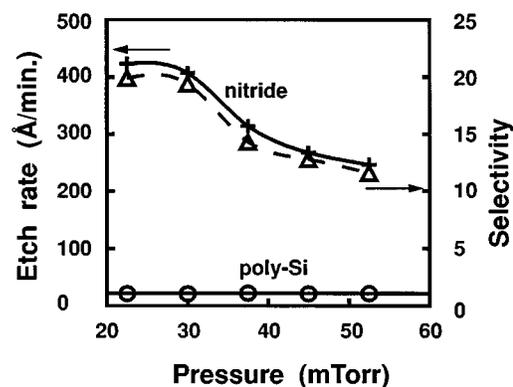


FIG. 3. Effects of pressure on the etch rates of nitride and polysilicon and the selectivity. Power=60 W,  $CHF_3=7.5$  sccm,  $N_2=42.5$  sccm.

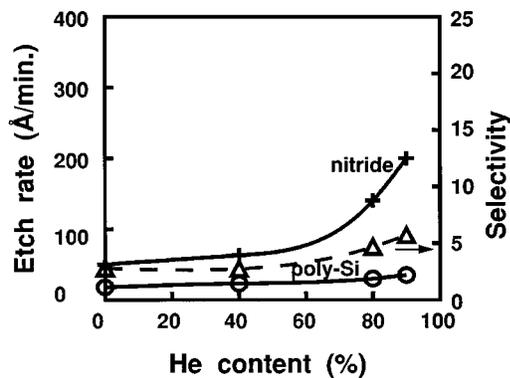


FIG. 4. Etch rates of polysilicon and silicon nitride and the selectivity vs He content in the  $\text{CHF}_3 + \text{He}$  chemistry. rf power=60 W, pressure=37.5 mTorr, the total flow rate=50 sccm.

the pressure and that the selectivity varies with the same trend because the etch rate of the polysilicon is not significantly influenced by the pressure.

### C. The effects of helium addition instead of $\text{N}_2$

For comparison helium was used in place of  $\text{N}_2$  as the additive gas to  $\text{CHF}_3$ . Helium is an inert gas and its role is mainly dilution, in addition to changing the electron energy distribution function. Figure 4 shows the etch rate of the nitride and polysilicon and the selectivity versus He content. The rf power, gas pressure, and total gas flow rate were the same as those for Fig. 1. It can be seen that both etch rates for the nitride and polysilicon increase with the He content. The selectivity increases with the He content due to the fact that the nitride etch rate increases more compared to the polysilicon etch rate. The selectivity increase is similar to the results as in the case of  $\text{N}_2$  addition. However, the maximum selectivity (5.5 at 90% He content) is much less than that with the  $\text{N}_2$  addition (16).

### D. The effects of mask materials

In addition to photoresist, an aluminum film and a nitride layer were also used as mask material for the nitride and polysilicon etching. Table I lists the etch rates for the nitride and polysilicon and selectivity with all the three mask materials. It is shown that the etch rate for the nitride is basically not affected by the mask materials while that of polysilicon with the resist mask is lower than that with either the Al or nitride mask, leading to the highest selectivity among the

TABLE I. Effect of mask materials on the etch rate and selectivity of nitride etching over polysilicon. rf power=60 W, pressure=37.5 mTorr,  $\text{CHF}_3=7.5$  sccm,  $\text{N}_2=42.5$  sccm.

Mask	Etch rate ( $\text{\AA}/\text{min}$ )		Selectivity SiN/poly-Si
	Nitride	Polysilicon	
Resist	350	25	14
Al	350	100	3.5
Nitride	380	90	4.2

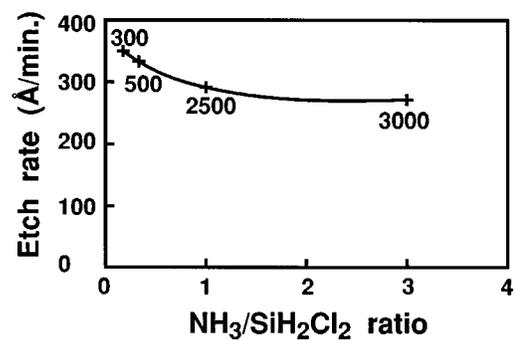


FIG. 5. Etch rate dependence of silicon nitride on the  $\text{NH}_3/\text{SiH}_2\text{Cl}_2$  flow rate ratio during deposition. The plasma etching conditions are: rf power=60 W, pressure=37.5 mTorr,  $\text{CHF}_3=7.5$  sccm,  $\text{N}_2=42.5$  sccm. The conditions for the LPCVD nitride deposition are: temperature=850 °C, pressure=150 mTorr, total flow rate of  $\text{SiH}_2\text{Cl}_2 + \text{NH}_3=200$  sccm. The values next to each data point are corresponding residual strain levels in  $\mu\epsilon$ .

three mask materials. The result implies that photoresist plays an important role in providing sufficient polymer-forming radicals to form the polymer film on the silicon substrate. Photoresist consists generally of resin which is a compound of carbon and hydrogen. During the plasma etching, photoresist is also etched by reactive species such as F atoms.<sup>16</sup> The carbon-containing reaction products can help the formation of C-F polymer film by providing more precursors in the reaction system.

### E. The effects of $\text{NH}_3/\text{SiH}_2\text{Cl}_2$ ratio during nitride deposition

To examine the effects of nitride composition (Si/N ratio) on the etching characteristics, the flow rate ratio of  $\text{NH}_3$  to  $\text{SiH}_2\text{Cl}_2$  for the LPCVD reaction is varied while keeping the total flow rate to a constant 200 sccm. The lower end of the ratio (30/170) results in a nitride film with a Si/N ratio of 0.82, while at the higher end of the ratio (150/50) a Si/N ratio of 0.73. Figure 5 shows the etch rate dependence on the  $\text{NH}_3/\text{SiH}_2\text{Cl}_2$  ratio, indicating that the etch rate decreases with increasing ratio.

### F. The effects of residual stress in the nitride film

Annealing at high temperature (>850 °C) can significantly increase the residual stress level in the nitride film, but does not change the Si/N ratio of the film.<sup>15</sup> To investigate the effect of the residual stress level on the nitride etch rate, an anneal was carried out at 850 and 1000 °C for 45 min in Ar atmosphere before the film was etched. The annealing results in a residual stress level of 400 and 1000  $\mu\text{strain}$ , respectively. It was found that there was no measurable difference in the etch rate between the as-deposited and the annealed films, indicating that the residual stress level does not influence the nitride etch rate.

## IV. DISCUSSIONS

### A. Etching mechanism

In a  $\text{CHF}_3$ -based plasma, ionization processes as a result of energetic electron collisions produce reactive species such as F atoms,  $\text{CF}_2$  radicals, and  $\text{CHF}_2^+$  ions, which react with the nitride when adsorbing on the nitride surface. The detailed etching mechanisms have been investigated.<sup>14,17</sup> The silicon nitride is mainly etched by F radicals via ion-assisted surface reactions. The observed very low etch rate of polysilicon is due to surface polymerization resulting from  $\text{CF}_2$  radicals, and thus a high selectivity of the nitride (or oxide) etching over polysilicon is obtained.

Energetic ion bombardment plays a key role in enhancing the nitride reactions as well as preventing polymerization on nitride surface. This argument is supported by the results in Figs. 2 and 3, showing that with either higher power or lower pressure the etch rate for the nitride is increased. Higher power produces higher potential difference between the plasma and substrate and lower pressure results in a longer mean-free path of ions. As a result, the kinetic energy of ions which bombard the substrate surface increases.

The formation of the C–F polymer film on the silicon substrate is confirmed by the experiment of polysilicon/polysilicon contact through windows in a nitride insulating layer.<sup>18</sup> When nitride is etched using the highly selective chemistry of 5 sccm  $\text{CHF}_3$ +45 sccm  $\text{N}_2$  at 60 W and 37.5 mTorr, a very high contact resistance ( $>10^{12} \Omega$ ) is observed on  $4 \times 4 \mu\text{m}^2$  windows between the two polysilicon layers. If a postetching cleaning process is applied which uses 50 sccm  $\text{O}_2$  plasma processing in the same reactor, the contact resistance is dramatically reduced to about 90  $\Omega$ . The high contact resistance appears to be caused by the C–F polymer layer according to the discussion above. This film can be effectively removed in the  $\text{O}_2$  plasma.

### B. Role of $\text{N}_2$ addition

A direct effect of  $\text{N}_2$  addition is the dilution. It has been pointed out that  $\text{N}_2$  plays a very minor chemical role in fluorocarbon plasmas and can be thought of as essentially a diluent gas.<sup>19</sup> The dilution lowers the concentration of polymer-forming radicals and, therefore, decreases the thickness of the etch-retarding polymer film and enhances the etch rate. Another important effect of  $\text{N}_2$  addition is to enhance dissociation/ionization processes of  $\text{CHF}_3$ ,<sup>20</sup> due to a change in the electron energy distribution function.<sup>21</sup>

Furthermore, there might be some additional mechanisms responsible for the rapid increase of nitride etch rate with  $\text{N}_2$  content. Note, that apart from the surface polymerization, another rate-limiting process during the nitride etching is the desorption of N atoms adsorbed on the surface, which are left as a result of reaction of silicon with, for example, F atoms and subsequent  $\text{SiF}_2$  desorption.<sup>14</sup> The distance between the N atoms in the LPCVD nitride ranges between 2.7 and 3 Å,<sup>22</sup> which is larger than that in a  $\text{N}_2$  molecule (a N–N single bond distance, which is in the order of 1.5 Å). Therefore the adsorbed N atoms are not likely to spontaneously combine with each other to form volatile  $\text{N}_2$  molecules. The argument is supported by the experimental results shown in

Fig. 5, where the etch rate of the nitride decreases with increasing  $\text{NH}_3/\text{SiH}_2\text{Cl}_2$  ratio, i.e., with increasing nitrogen composition in the nitride film.

When  $\text{N}_2$  is added to the  $\text{CHF}_3$ , abundant nitrogen atoms are generated. The nitrogen atoms can diffuse to the substrate surface and combine with the nitrogen atoms adsorbed there with the help of ion bombardment, forming volatile  $\text{N}_2$  molecules and therefore increasing etching rate of the nitride.

Because of the significant increase of the nitride etch rate with the  $\text{N}_2$  content compared to the moderate increase with the He addition, it is suggested that the diffusion and combination of the nitrogen atoms produced by dissociation of  $\text{N}_2$  is a major factor which enhances the reaction in addition to the dilution effects.

## V. CONCLUSIONS

Effects of  $\text{N}_2$  addition to  $\text{CHF}_3$  plasma as well as rf power and gas pressure on the etch rate of silicon nitride, silicon dioxide, and selectivity of the nitride over polysilicon have been examined and compared with that of He addition. Photoresist, Al film and nitride have been used for the etch mask. Various kinds of nitride films with different Si/N composition and residual stress level have been etched using the  $\text{CHF}_3/\text{N}_2$  chemistry. It was found that the etch rate for the nitride increased sharply with the  $\text{N}_2$  addition and moderately with the He addition, while that of the polysilicon was essentially not changed, resulting in a maximum selectivity of 16 with 42.5 sccm  $\text{N}_2$  added to 7.5 sccm  $\text{CHF}_3$  (85%  $\text{N}_2$  content) at 60 W and 37.5 mTorr. Higher power or lower pressure tends to increase the nitride etch rate but does not change the polysilicon etch rate significantly. The nitride etch rate was found to be independent of the mask materials, while that of the polysilicon was higher with the Al or nitride mask than with the resist mask. The etch rate for the nitride which consists of more nitrogen was lower than that which consists of less nitrogen. Residual stress level was found to have little influence on the nitride etch rate.

The results, in combination with the analysis of the nitride structures, suggest that desorption of nitrogen atoms from the substrate and polymer film formation are two major rate-limiting factors in the nitride etching and photoresist plays an important role in providing sufficient polymer-forming radicals to ensure high selectivity over the polysilicon. It is argued that the addition of nitrogen gas to  $\text{CHF}_3$  has a twofold role in the etching of the nitride. The first is dilution of the polymer-forming radicals and the second is generation of nitrogen atoms which diffuse to the substrate and combine with the nitrogen atoms, which are adsorbed there as a result of reaction of silicon atoms with reactive radicals. Both factors enhance the nitride etching in the plasma system.

## ACKNOWLEDGMENTS

The authors are indebted to the staff of Delft Institute of Microelectronics and Submicronotechnology (DIMES), especially Dr. P. M. Sarro, for their assistance in the sample preparation.

- <sup>1</sup>K. E. Petersen, Proc. IEEE **70**, 420 (1982).
- <sup>2</sup>R. F. Wolffenbuttel, J. F. L. Goosen, and P. M. Sarro, Sensors and Actuators A **25–27**, 583 (1991).
- <sup>3</sup>M. R. Wolffenbuttel, Y. X. Li, D. Poenar, P. J. French, P. P. L. Regtien, and R. F. Wolffenbuttel, Proceedings of the 7th International Conference on Solid-State Sensors and Actuators, Yokohama, Japan, June 7–10, 1993, p. 284.
- <sup>4</sup>T. C. Mele, J. Nulman, and J. P. Krusius, J. Vac. Sci. Technol. B **2**, 684 (1984).
- <sup>5</sup>T. Kure, Y. Kawamoto, N. Hashimoto, and T. Takaichi, Technical Digest of 1983 International Electron Device Meeting, U.S.A., p. 757.
- <sup>6</sup>H. W. Lehmann and R. Widmer, J. Vac. Sci. Technol. **15**, 319 (1978).
- <sup>7</sup>J. L. Linstrom, G. S. Oehrlein, and W. A. Lanford, J. Electrochem. Soc. **139**, 317 (1992).
- <sup>8</sup>H. Norstrom, R. Buchta, F. Ronovc, and P. Wiklund, Vacuum **32**, 737 (1982).
- <sup>9</sup>L. M. Loewenstein, J. Vac. Sci. Technol. A **7**, 686 (1989).
- <sup>10</sup>H. Boyd and M. S. Tang, Solid State Technol. **22**, 133 (1979).
- <sup>11</sup>S. Matsuo, Jpn. J. Appl. Phys. **17**, 235 (1978).
- <sup>12</sup>S. Matsuo, J. Vac. Sci. Technol. **17**, 587 (1980).
- <sup>13</sup>R. A. H. Heineke, Solid-State Electron. **18**, 1146 (1975).
- <sup>14</sup>P. E. Clarke, D. Field, A. J. Hydes, D. F. Klemperer, and M. J. Seakins, J. Vac. Sci. Technol. B **3**, 1614 (1985).
- <sup>15</sup>P. J. French, R. F. Wolffenbuttel, R. Mallee, and P. M. Sarro, The Book of Abstract of EUROSENSORS VIII Conference, Toulouse, France, Sept. 25–28, 1994, p. 205.
- <sup>16</sup>D. L. Flamm, in *Plasma Etching—An Introduction*, edited by D. M. Maros and D. L. Flamm (Academic, San Diego, 1989), Chap. 2, pp. 91–184.
- <sup>17</sup>J. Dulak, B. J. Howard, and Ch. Steinbyuchel, J. Vac. Sci. Technol. A **9**, 775 (1991).
- <sup>18</sup>Y. X. Li, P. J. French, and R. F. Wolffenbuttel, IEEE Trans. Electron Devices **48**, 64 (1995).
- <sup>19</sup>J. W. Coburn and E. Kay, Solid State Technol. **22**, 117 (1979).
- <sup>20</sup>Y. Miyakawa, J. Hashimoto, N. Ikegami, and J. Kanamoro, Mater. Res. Soc. Symp. Proc. **279**, 813 (1992).
- <sup>21</sup>M. Sato and H. Nakamura, J. Electrochem. Soc. **129**, 2522 (1982).
- <sup>22</sup>V. I. Belyi, L. L. Vasilyeva, and A. S. Ginovker, *Silicon Nitride in Electronics* (Elsevier, Amsterdam, 1988), Vol. 34, Chap. 4.