

Film properties of nitrogen-doped polycrystalline silicon for advanced gate material

Sang Ho Woo*, Yil Wook Kim**, Pyung Yong Um**, Hae-Min Lee*, and Chang-Koo Kim**†

*Department of Chemical Engineering and Division of Energy Systems Research, Ajou University, San 5 Woncheon-dong, Yeongtong-gu, Suwon 443-749, Korea

**Eugene Technology Co. Ltd., 209-3 Chuge-ri, Yangji-myun, Yongin 449-824, Korea

(Received 26 August 2008 • accepted 12 November 2008)

Abstract—Deposition of N-doped poly-Si films from SiH_4 and NH_3 using a single wafer type low pressure chemical vapor deposition (LPCVD) system was investigated to improve the grain size reduction and the grain size distribution. The deposition rate and surface roughness of N-doped Si were greatly affected by the NH_3/SiH_4 ratio such that they decreased with increasing NH_3/SiH_4 ratio. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements revealed that with increasing NH_3/SiH_4 ratio, the size of the grains was decreased and the grains size distribution became uniform. Finally, we successfully obtained N-doped poly-Si films having uniform grain size of approximately 6 nm.

Key words: N-doped Si, Low Pressure Chemical Vapor Deposition, Grain Size, Surface Roughness

INTRODUCTION

Polycrystalline silicon (poly-Si) is widely used as floating gate material for flash memory devices because of its good capability for programming and erase performance [1,2]. As the dimensions of such devices keep shrinking, the degree of device integration has been dramatically increased. Thus, the performance of the devices depends critically on film properties such as surface morphology and grain size distribution. In particular, it is strongly required that a poly-Si gate has a uniform grain size distribution through the entire film stack to keep endurance and reliability of the devices [3,4]. Muramatsu et al. [5] proposed that oxide valleys in the tunnel oxide play an important role in erase speed of flash memory devices. They pointed out that many grains exist in each erase area when the size of grains in poly-Si is small, resulting in a narrow distribution of erase threshold voltage.

Efforts have been made to deposit poly-Si having small sized grains. Among them, the addition of impurities to poly-Si films is one of the candidates to reduce grain size of the films. Luoh et al. [1] reported on micrograin poly-Si using a single wafer processor with hydrogen addition. They obtained grain size as low as 5 nm. Togo et al. [6] utilized ion implantation to add nitrogen into poly-Si. They found that nitrogen implantation into poly-Si reduced the grain size of poly-Si, resulting in suppression of gate leakage current. However, ion implantation may cause severe damage to tunnel oxide when the thickness of poly-Si is very thin.

In this work, improvement of the grain size distribution and morphology of poly-Si was investigated by using nitrogen (N)-doped poly-Si deposited in a single wafer type LPCVD (low pressure chemical vapor deposition) system.

EXPERIMENTAL

N-doped Si was deposited in a commercial single wafer LPCVD

system (Eugene Technology, Model: BJM1000) [7]. The LPCVD system had a unique shower head assembly to improve the uniformity of gas distribution. Side vacuum plates were also attached on the edge of the chamber to obtain a better distribution of gas flow over a process wafer.

Samples were 300 mm Si (100) wafers having thermally grown oxide (100 nm thick) on top of them. Silane (SiH_4) and ammonia (NH_3) were used as sources for Si and N, respectively. The flow rate of SiH_4 was fixed at 100 sccm and the NH_3 flow rate was varied from 0 to 1.7 sccm. Deposition temperature and pressure were maintained at 700 °C and 25 Torr, respectively, throughout the experiments.

The deposition rates were determined by measuring changes in the thickness after deposition by using a thickness meter (Filmetrics, Model: F50). The concentration of nitrogen in N-doped Si was obtained by depth profiling with SIMS (secondary ion mass spectroscopy, Cameca, Model: IMS-6f). After deposition, morphological and structural studies were performed by AFM (Atomic Force Micros-

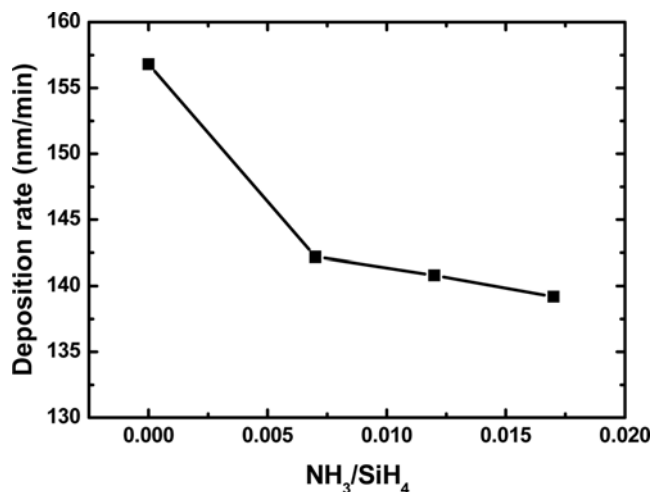


Fig. 1. Deposition rate of N-doped Si as a function of NH_3/SiH_4 ratio.

†To whom correspondence should be addressed.

E-mail: changkoo@ajou.ac.kr

copy, Veeco, Model: D3100), XRD (X-Ray Diffraction, Rigaku, Model: D/MSX-RC), and TEM (Transmission Electron Microscopy, FEI, Model: Tennai F30 Super Twin).

RESULTS AND DISCUSSION

Fig. 1 shows the deposition rate of N-doped Si as a function of NH_3/SiH_4 ratio. In the absence of NH_3 , the deposition rate of Si was as high as 156 nm/min. The deposition rate decreased monotonically with increasing NH_3/SiH_4 ratio. When SiH_4 is used to deposit Si films, it is well known that the pyrolysis of SiH_4 results in the formation of silylene (SiH_2) and the heterogeneous reaction between SiH_2 and the solid surface produces Si such that [8]



In the presence of NH_3 , NH_3 reacts with SiH_4 to form silylamine (SiH_3NH_2) and hydrogen gas [9]. As the amount of NH_3 is increased, the concentration of hydrogen in the gas phase increases. It inhibits the pyrolysis of SiH_4 , which finally leads to a decrease in the de-

position rate of Si [10].

The concentration of N in the Si films was obtained by depth profiling with SIMS. Fig. 2 shows the relative concentration of N in the Si films as NH_3/SiH_4 ratio is varied. It is seen that N concentration increases with NH_3/SiH_4 ratio. As mentioned earlier, SiH_3NH_2 is produced when NH_3 is introduced in the course of Si deposition using SiH_4 . The formation of SiH_3NH_2 results in the deposition of N atoms into the film. NH_3 also leads to the deposition of N atoms by direct decomposition. Therefore, the concentration of N in the Si films increases with NH_3/SiH_4 ratio.

Fig. 3 shows the AFM images of Si films without and with NH_3 addition. It is seen that the addition of NH_3 (1.7 sccm) produced a smoother Si surface compared to that without NH_3 . For better comparison, the surface roughness of the N-doped Si films was obtained by using AFM.

Fig. 4 illustrates the dependence of surface roughness on the NH_3/SiH_4 ratio. The behavior of the surface roughness with NH_3/SiH_4 ratio follows similar variation to the deposition rate, i.e., the surface roughness of the N-doped Si films decreases with increasing NH_3/SiH_4 ratio. Therefore, it can be said that the surface roughness of N-doped Si is more prominently affected by the deposition kinet-

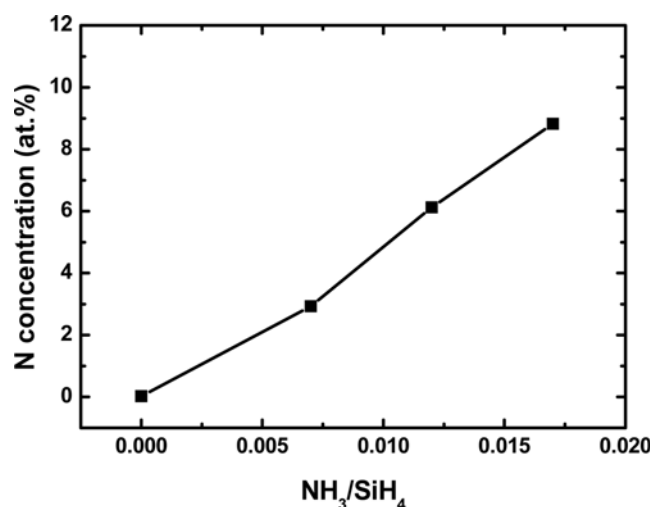


Fig. 2. Concentration of nitrogen in the Si films as a function of NH_3/SiH_4 ratio.

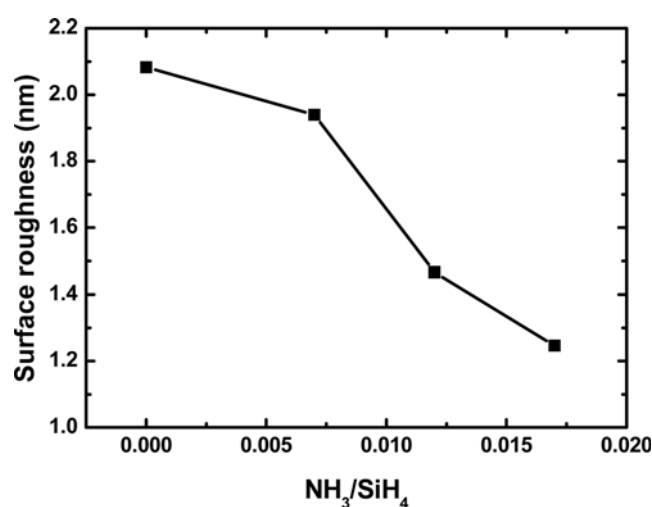


Fig. 4. Dependence of surface roughness of N-doped Si on NH_3/SiH_4 ratio.

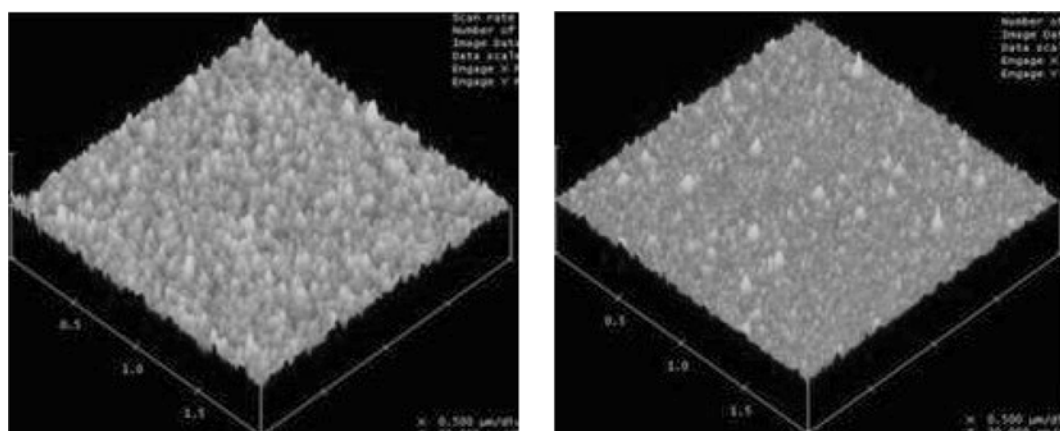
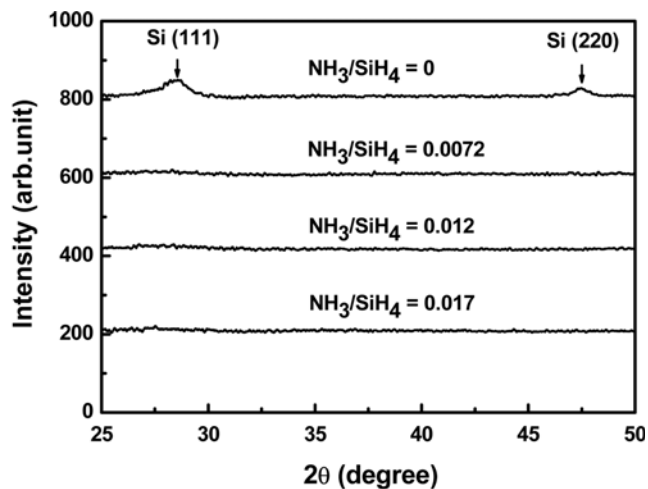
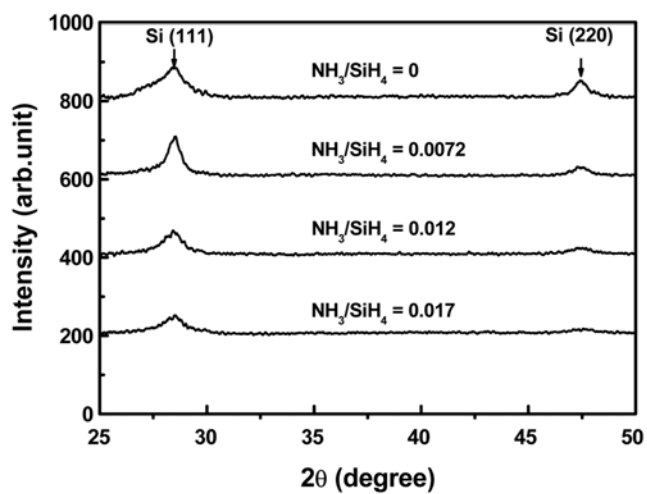


Fig. 3. AFM images of Si films (a) without and (b) with NH_3 addition. In (b), NH_3 of 1.7 sccm was added during the film deposition.



(a)



(b)

Fig. 5. X-Ray diffraction patterns of Si films (a) as-deposited and (b) after annealing at 840 °C for 40 min.

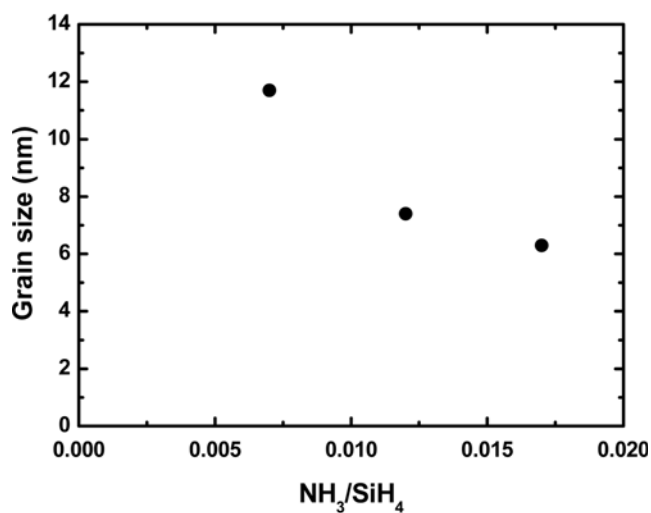
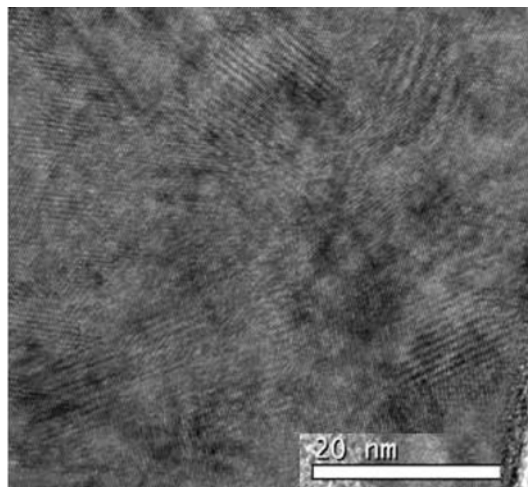
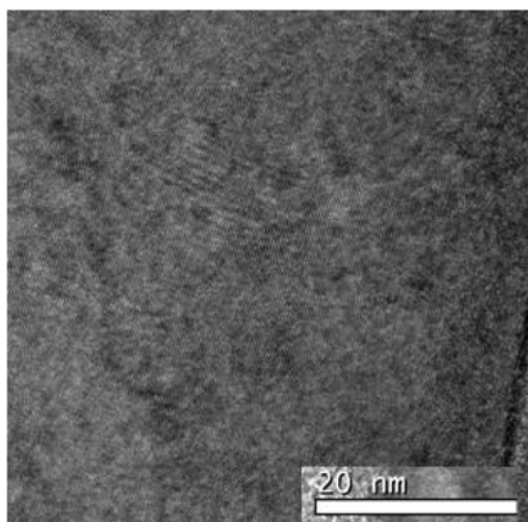


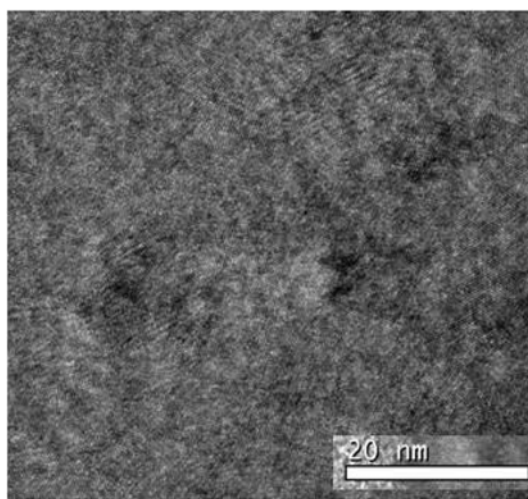
Fig. 6. Dependence of grain size of N-doped Si on NH_3/SiH_4 ratio after annealing at 840 °C for 40 min.



(a)



(b)



(c)

Fig. 7. TEM images of N-doped Si after annealing at 840 °C for 40 min. The NH_3/SiH_4 ratio was (a) 0.007, (b) 0.012, and (c) 0.017.

ics rather than microstructure.

Fig. 5 shows XRD patterns of Si films (a) as-deposited and (b) after annealing at 840 °C for 40 min. Without NH₃, the XRD pattern of as-deposited Si shows typical polycrystalline structure having peaks at $2\theta=28.45^\circ$ and 47.30° , which are from Si with directions of (111) and (220), respectively. When NH₃ is introduced, however, no distinct peaks are seen from XRD patterns of as-deposited N-doped Si. These results suggest that N doping into Si films prevents them from forming crystalline structures. On annealing at 840 °C, XRD spectra of Si show that peaks are stronger than those from as-deposited Si. Over the NH₃ concentration range employed in this work (0.7-1.7 sccm), the peak intensities become smaller with increasing the amount of NH₃, confirming that crystallization of Si films is inhibited by N doping.

Using XRD spectra, the average grain size can be calculated by Scherrer's formula [11]. Fig. 6 shows the dependence of grain size of N-doped Si on NH₃/SiH₄ ratio. In this case, grains with only (111) direction were considered because the XRD peaks of (220) direction were too small to be differentiated. The grain size ranged below 13 nm and decreased with increasing NH₃/SiH₄ ratio. Especially, we successfully obtained N-doped Si films having grain size of approximately 6 nm.

The grain size distribution was investigated by TEM measurements. Fig. 7 shows the TEM images of N-doped Si after annealing at 840 °C. In the presence of NH₃, N-doped Si has a fairly good distribution of the grain size. One can also see that smaller size grains produce a better distribution.

CONCLUSIONS

N-doped Si was deposited from SiH₄ and NH₃ by using a single wafer type LPCVD system. The deposition rate of N-doped Si was decreased with increasing NH₃/SiH₄ ratio since the introduction of NH₃ inhibited the pyrolysis of SiH₄. The surface roughness of N-doped Si was also decreased with NH₃/SiH₄ ratio, implying that the surface roughness of N-doped Si would be strongly affected by

the deposition kinetics rather than microstructure. XRD and TEM measurements revealed that with increasing NH₃/SiH₄ ratio, the size of the grains was decreased and the grain size distribution became uniform. Finally, we obtained N-doped Si films having a uniform grain size of approximately 6 nm.

ACKNOWLEDGMENT

This work was supported by Eugene Technology Co., Ltd. and an Ajou University Research Fellowship 2007 (Grant No. 20072650).

REFERENCES

1. T. Luoh, T.-T. Han, Y.-C. Yang, K.-C. Chen, H.-H. Shih, Y.-L. Hwang and C.-C. Hsueh, *IEEE Trans. Semicond. Manuf.*, **16**, 155 (2003).
2. Y. S. Song and C. W. Chung, *Korean J. Chem. Eng.*, **20**, 1138 (2003).
3. S. Mori, Y. Yamaguchi, M. Sato, H. Meguro, H. Tsunda, E. Kamiya, K. Yoshikawa, N. Arai and E. Sakagami, *IEEE Trans. Electron Devices*, **43**, 47 (1996).
4. F. D. Nkansah and M. Hatalis, *IEEE Trans. Electron Devices*, **46**, 1355 (1999).
5. S. Muramatsu, T. Kubota, N. Nishio, H. Shirai, M. Matsuo, N. Kodama, M. Horikawa, S. Saito, K. Arai and T. Okazawa, *IEDM Tech. Dig.*, 847 (1994).
6. M. Togo, T. Suzuki, E. Hasegawa, S. Koyama, T. Fukai, A. Sakakidani, S. Miyake, T. Watanabe, I. Yamamoto, M. Tanaka, Y. Kawashima, Y. Kunimune, M. Ikeda and K. Imai, 2006 Symp. *VLSI Tech. Dig. Technical Papers*, 30 (2006).
7. P. Y. Um, Korean patent, 10-2004-0063047 (2004).
8. R. F. C. Farrow, *J. Electrochem. Soc.*, **121**, 899 (1974).
9. P. Temple-Boyer, L. Jalabert, L. Masarotto, J. L. Alay and J. R. Morante, *J. Vac. Sci. Technol. A*, **18**, 2389 (2000).
10. E. Scheid, L. K. Kouassi, R. Henda, J. Samitier and J. R. Morante, *Mater. Sci. Eng. B*, **17**, 72 (1993).
11. B. D. Cullity, in *Elements of X-ray diffraction*, M. Cohen, Editor, Addison-Wesley, Reading, MA (1978).