Heavy arsenic doping of silicon grown by atmospheric pressure selective epitaxial chemical vapor deposition

Tetsuya Ikuta\textsuperscript{a,b,*}, Yuki Miyanami\textsuperscript{a}, Shigeru Fujita\textsuperscript{a}, Hayato Iwamoto\textsuperscript{a}, Shingo Kadomura\textsuperscript{a}, Takayoshi Shimura\textsuperscript{b}, Heiji Watanabe\textsuperscript{b}, Kiyoshi Yasutake\textsuperscript{b}

\textsuperscript{a}Semiconductor Technology Development Group, Semiconductor Business Unit, Sony Corporation, 4-14-1 Asahi-cho, Atsugi, Kanagawa 243-0014, Japan
\textsuperscript{b}Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Received 30 October 2006; received in revised form 18 January 2007; accepted 6 February 2007
Available online 26 March 2007

Abstract

Selective epitaxial Si with a high arsenic concentration of \(2.2 \times 10^{19}\) atoms/cm\(^3\) was deposited at a high growth rate of 3.3 nm/min under atmospheric pressure. It was confirmed that this method had excellent selectivity and produced films having good crystalline quality, abrupt dopant profiles at the interfaces, and smooth surfaces. The growth mechanism is discussed in terms of the relationship between the effects of arsenic surface segregation and etching by hydrogen chloride.

\(\text{R}^2\) 2007 NIMS and Elsevier Ltd. All rights reserved.

Keywords: As; Si; Atmospheric pressure; Chemical vapor deposition; In situ doping; Selective epitaxial growth; Raised extension; Segregation; Etching

1. Introduction

Recently, the scalability of metal-oxide-semiconductor field effect transistors (MOSFETs) for the 45-nm technology node and beyond has been discussed. One of the critical issues is suppression of the short-channel effect (SCE) caused by shrinking dimensions. Reducing the extension junction depth and the raised extension structure are effective approaches for suppressing SCE. The in situ doped selective epitaxial growth (SEG) process has been investigated as a method for producing such structures [1–4]. This process produces an abrupt dopant profile at the junction interface since it does not use activation annealing.

There have been many attempts to perform heavy arsenic doping into Si because of its high solubility and its small diffusion coefficient. However, highly doped films have not been realized due to the strong surface segregation of As atoms during growth, which is caused by the formation of symmetric As dimers with no dangling bond on the Si(001) surface, and reduces the surface energy significantly [5]. The surface segregation prevents the incorporation of As into the film, and the segregated As atoms passivate the growth surface, reducing the growth rate [5–8].

In this study, we investigated the possibility of using in situ doped Si SEG under atmospheric pressure (AP) to overcome these problems. We also discuss the growth mechanism on the basis of the surface segregation of As and the effects of etching by hydrogen chloride.

2. Experimental

All films were grown in a cold-wall reduced-pressure chemical vapor deposition reactor. The substrates were p-type CZ Si(100) wafers that were 200 mm in diameter and had a resistivity of 8–12 \(\Omega\)cm. The selectivity was confirmed by growing films on the patterned substrate with standard MOSFET structures which included Si, SiN, and SiO\(_2\) surfaces. The wafers were cleaned with HF, then in situ \(H_2\) annealing was performed. The precursor gases of \(\text{SiH}_2\text{Cl}_2\), HCl, and AsH\(_3\) were used for the in situ As-doped Si SEG. Hydrogen with a flow rate of 20 slm was used as the carrier gas. In the present study, the ratio of the flow rates of \(\text{SiH}_2\text{Cl}_2\) to HCl was 2. The flow rates of AsH\(_3\),...
diluted to 1% in hydrogen were varied from 0.6 to 10 sccm for in situ doping. The total pressure was controlled to be AP or a low pressure (LP) of 10 torr using a conductance valve which was mounted between the chemical vapor deposition chamber and the vacuum pump. The substrates were kept at 750°C during growth.

The selectivity was observed by scanning electron microscopy (SEM), while the crystalline quality of the film was examined by transmission electron microscopy (TEM). The depth profile of the As concentration was measured by secondary ion mass spectrometry (SIMS) and the surface roughness was estimated using an atomic force microscope (AFM). The concentration of As atoms located at substitutional sites was estimated from the resistivity using the Irvin curve [9,10].

3. Results and discussion

3.1. Characterization of atmospheric in situ As-doped Si SEG

Fig. 1 shows a top view of a patterned substrate with a MOSFET structure obtained by SEM. The shallow trench isolation (STI) is formed by SiO₂ and the top of the gate electrode is covered by Si₃N₄. We confirmed that the epitaxial layers were grown only on the Si surface and not on the Si₃N₄ and SiO₂ surfaces of the STI and the gate areas, respectively. This means that atmospheric in situ As-doped Si SEG has good selectivity.

Fig. 2 shows a typical cross-sectional TEM image. We observed no defects in the film. This demonstrates that the film had good crystalline quality.

Fig. 3 shows the As depth profile measured by SIMS. In this sample, the As concentration is $2.2 \times 10^{19}$ atoms/cm³. The As concentration is uniform throughout the film and changes abruptly at the interface. The junction depth was estimated to be 5 nm at a concentration of $5 \times 10^{18}$ atoms/cm³, which is sufficiently small to suppress the SCE.

Figs. 4(a) and (b) show AFM images of the surfaces of Si layers grown under LP and AP, respectively. The root mean square roughness of the Si layer grown under AP is half that grown under LP.

The As concentrations and activation ratios are plotted in Figs. 5(a) and (b) as a function of the AsH₃ flow rate,
respectively. This figure shows that films grown under AP have better As concentrations than those grown under LP and that for both pressures the As concentration increases as the AsH₃ flow rate increases. The As concentration in the film grown under AP is 7 times higher than that in the film grown under LP. Furthermore, although the activation ratio decreases as the AsH₃ flow rate increases for growth under LP, it increases for growth under AP.

The growth rates are plotted in Fig. 6 as a function of the AsH₃ flow rate. The growth rate under LP decreases as the AsH₃ flow rate increases. Surprisingly it increases under AP. The growth rate under AP is 17 times higher than that under LP at a AsH₃ flow rate of 10 sccm.

### 3.2. Growth mechanism

In previous studies, it has proved difficult to grow epitaxial Si layers having high As concentrations at high growth rates because As atoms segregate at the growth surface. Increasing the AsH₃ flow rate results in low growth rates and a rough surface because of the passivation of the growth surface by the segregated As atoms [11–16]. However, we were able to grow highly As-doped films at a high growth rate by increasing the growth pressure to AP.

It is important to investigate the effects of HCl etching on the growth rate and As surface segregation in order to explain this unexpected result with respect to the growth rate under AP. First, we determined the growth rates for undoped SEG and found them to be 6.6 and 4.3 nm/min under LP and AP, respectively. As expected, these values are much higher than those for doped SEG, but it should be noted that the growth rate under AP is lower than that under LP. This indicates that etching by HCl is more effective under AP than under LP because, when HCl and AsH₃ gases are not present, the growth rate under AP is higher than that under LP. In other words, more Si atoms are etched by HCl under AP than under LP.

In order to investigate the difference in the etching rates for Si and As atoms, the total As concentration was measured as a function of the HCl flow rate, together with the concentration of the substitutional As atoms (see Fig. 7). The As concentration decreases as the HCl flow rate increases, indicating the higher etching rate of As atoms than that of Si atoms. The substitutional As concentration remains constant as the HCl flow rate is increased, while the interstitial As concentration decreases. This means that interstitial As atoms are preferentially etched by HCl over the substitutional As atoms.

Based on these results, the characteristic features of AP in situ doped SEG are interpreted in terms of the effects of As surface segregation and etching by HCl. The high growth rate obtained under AP is due to the enhanced etching of As atoms by HCl, which suppresses As surface segregation. Increasing the AsH₃ flow rate suppresses the etching of Si atoms by HCl, because As atoms are preferentially etched over Si atoms, resulting in higher...
growth rates. The smooth surface is also a result of the suppression of As surface segregation caused by etching by HCl. The increase in the activation ratio is a consequence of the selective etching of the interstitial As atoms.

4. Conclusion

We investigated atmospheric in situ As-doped Si SEG, which gave a high As concentration of $2.2 \times 10^{19}$ atoms/cm$^3$ and a high growth rate of 3.3 nm/min. It was confirmed that this method had excellent selectivity and produced films having good crystalline quality, abrupt dopant profiles at the interfaces, and smooth surfaces. These effects were interpreted in terms of enhanced etching by HCl under AP.

Acknowledgments

The authors would like to thank Mr. Kawamura and Mr. Asakawa of Osaka University for their technical support.

References

[1] J. Wang, Y. Kikuchi, Y. Tateshita, T. Kato, T. Kataoka, T. Hirano, K. Nagano, T. Ikuta, Y. Miyanami, S. Fujita, S. Hiyama, R. Yamamoto, S. Kanda, S. Yamakawa, T. Kimura, K. Kugimiya, N. Yamagishi, Y. Tagawa, Y. Kamide, H. Iwamoto, T. Ohno, M. Saito, S. Kadmura, N. Nagashima, in: Symposium on VLSI Technology Digest of Technical Papers, 2006, p. 238.
[2] Y. Tateshita, T. Imoto, Y. Kikuchi, J. Wang, T. Kataoka, Y. Miyanami, H. Ikeda, S. Fujita, T. Landin, C. Arena, H. Iwamoto, T. Ohno, T. Kobayashi, M. Saito, S. Kadmura, N. Nagashima, in: Extended Abstract of the International Conference on Solid State Devices and Materials, 2005, p. 904.
[3] N. Yasutake, K. Ohuchi, M. Fujiwara, K. Adachi, A. Hokazono, K. Kojima, N. Aoki, H. Suto, T. Watanabe, T. Morooka, H. Mizuno, S. Magoshi, T. Shimizu, S. Mori, H. Oguma, T. Sasaki, M. Ohmura, K. Miyano, H. Yamada, H. Tomita, D. Matsushita, K. Muraoka, S. Inaba, M. Takayanagi, K. Ishimaru, H. Ishiuchi, in: Symposium on VLSI Technology Digest of Technical Papers 2004, pp. 84.
[4] H. Wakabayashi, T. Tatsumi, N. Ikarashi, M. Oshima, H. Kawamoto, N. Ikekawa, T. Ikezawa, T. Yamamoto, M. Hane, Y. Mochizuki, T. Mogami, in: International Electron Devices Meeting Technical Digest 2005, p. 151.
[5] X. Liu, Q. Tang, J.S. Harris, T.I. Kamins, J. Crystal Growth 281 (2005) 334.
[6] X. Liu, Q. Tang, T.I. Kamins, J.S. Harris, J. Crystal Growth 251 (2003) 651.
[7] M.H. Xie, A.K. Lees, J.M. Fernandez, J. Zhang, B.A. Joyce, J. Crystal Growth 173 (1997) 336.
[8] A.D. Hartell, E.S. Tok, J. Zhang, J. Crystal Growth 227 (2001) 729.
[9] F. Mousty, P. Ostoja, L. Passari, J. Appl. Phys. 45 (1974) 4576.
[10] R.B. Fair, G.R. Weber, J. Appl. Phys. 44 (1973) 280.
[11] T. Ohno, Phys. Rev. Lett. 73 (1994) 460.
[12] E.S. Tok, N.J. Woods, J. Zhang, J. Crystal Growth 209 (2000) 321.
[13] S. Fukatsu, K. Fujita, H. Yaguchi, Y. Shiraki, R. Ito, Appl. Phys. Lett. 59 (1991) 2103.
[14] P.C. Zalm, G.F.A. van de Walle, D.J. Gravesteijn, A.A. van Gorkum, Appl. Phys. Lett. 55 (1989) 2520.
[15] M. Copel, M.C. Reuter, E. Kaxiras, R.M. Tromp, Phys. Rev. Lett. 63 (1989) 632.
[16] R.I.G. Uhrberg, R.D. Bringans, R.Z. Bachrach, J.E. Northrup, Phys. Rev. Lett. 56 (1986) 520.