Extended Abstracts of the 22nd (1990 International) Conference on Solid State Devices and Materials, Sendai, 1990, pp. 445-448

C-10-10

Slow/Rapid Diffusion of Arsenic in SiO₂

Yoshitaka TSUNASHIMA, Takashi NAKAO, Kenji TODORI, and Kikuo YAMABE

ULSI Research Center, TOSHIBA Co. 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

The As diffusion in SiO₂ had been investigated by using ASSG film. As diffusivities and chemical states in SiO₂ are different for N₂ and H₂+N₂ annealing ambients. In N₂, the chemical state is not changed from that of as deposited film, and it is the oxidized state with a large diffusivity. On the contrary, As has been changed to the reduced state with a small diffusivity by a H₂+N₂ annealing. This chemical state transition is a reversible reaction. The diffusion mechanism is assumed to be a substitutional change with Si atoms of the SiO₂ network for the oxidized state As and an interstitial diffusion for the reduced state As.

1. INTRODUCTION

Solid phase diffusion, using a doped oxide as a diffusion source, attracts attention currently for a method to form a comformable doped layer on a threedimensional structure. Particularly, As-doped oxide (Arsenosilicate Glass; AsSG) had been applied to sidewall doping for the trench capacitor in Mbit DRAM's^{1,2)}. To control AsSG diffusion precisely, the authors had studied As diffusion behavior in the glass and As precipitation phenomenon caused at the glass/Si interface³⁾. However As diffusion mechanism in SiO₂ is still unknown.

Gezzo et al. reviewed previous works for As diffusion in SiO₂, which were using AsSG or AsH₃ for a dopant source⁴⁾. But these data are scattered in a wide range. Recently, diffusion of ion implanted As in SiO₂ were studied by many investigators⁵⁻¹⁰⁾. N₂/O₂ ambient dependency was discussed, and fast diffusion species were found⁹⁻¹⁰⁾. These experiments, however, cannot eliminate the influence of implanted damages.

In present work, As diffusion in SiO_2 are investigated by using AsSG films and correlated with As chemical states to presume

the diffusion mechanism. Mainly, the annealing ambient dependency of H_2/N_2 , which results quite different diffusion behavior, is studied in detail for the first time. 2. EXPERIMENTAL

AsSG films were deposited on (100) ptype Si using simultaneous thermal decomposition of TEOS (<u>Tetra-EthOxy-S</u>ilane) and TEOA (<u>Tri-EthOxy-Arsine</u>) in a hotwalltype LPCVD reactor. Typical film thickness was 100nm, and its As concentration was set in $10^{20}-10^{21}$ atoms/cm³ range. To study the As diffusion in AsSG, SiO₂/AsSG/SiO₂ stacked films, which were deposited on Si sequentially in the same reactor by TEOS with or without TEOA, were also used.

Diffusion annealing processes were carried out in temperature range $950-1050^{\circ}C$ for these samples. Three kinds of annealing ambient were used. An inert ambient; nitrogen (N₂), a reducing ambient; 10 percent H₂ contained N₂ (H₂+N₂), and an oxidizing ambient; 10 percent O₂ contained N₂ (O₂+N₂).

As distributions were analyzed with Secondary Ion Mass Spectrometry (SIMS). As chemical states in SiO_2 were investigated by X-ray induced Photoelectron Spectroscopy

(XPS) with SiO₂ wet-etching technique.
3. RESULTS AND DISCUSSION

Figure 1 shows As diffusion profiles Si substrate diffused from AsSG film at $1000^{\circ}C$ in H₂+N₂ and N₂, respectively. Initial As concentrations for as deposited AsSG films are the same, however diffusion profiles are quite different. For H2+N2, As diffusion profile is one order lower on surface shallower concentration and 70 nm in diffusion depth than usual N2 ambient. Also from the profiles for H_2+N_2 , As dose is not increasing with increasing annealing time from 1 to 4 hours. These results suggest that H2 had suppressed an As supply into Si. Arai et al. reported that sheet resistance was about 70 times larger for H_2 than for O_2 high concentration in AsSG annealing diffusion process¹¹⁾. Our observation will be the same phenomenon. Two factors originated with H2, could be considered to explain the results; a change in AsSG/Si interface property and a change in As diffusivity in SiO2. In this study, the latter had been investigated.

Figure 2 shows As profiles in $SiO_2/AsSG/SiO_2$ stacked films before and after annealing. According to $AsSG/SiO_2$ interfaces, As concentration decreases gradually from AsSG to SiO_2 for N_2 . On the contrary, the interface is abrupt and only little change from as deposited film can be observed for



Fig.1 As diffusion profiles in Si substrate, diffused from AsSG at $1000^{\circ}C$ in N₂ or H₂+N₂.

 H_2+N_2 . These profiles obviously suggest that As diffusion in SiO₂ has been suppressed by H₂ from the ambient. Using a simple error function approximation, diffusion profiles of the interface could be represented with good matching and As diffusivities were calculated. The same experiments had been accomplished in 950-1050°C temperature and 1-16 hours time range. Figure 3 shows Arrhenius plots for As diffusivities in SiO₂ for N₂ and Estimated Activation energies H2+N2. are 5.46eV for N₂ and 2.27eV for H2+N2, respectively. For N2, activation energy value is a little higher than those for ion implanted As (4.2-4.7eV), which had been reported by other workers 7,8). However, the diffusivity values are within the range of these reported values $^{6-9)}$, and the diffusion mechanism is assumed to be same.

From the diffusion behavior, As chemical state in SiO₂ must be different between for data^{ll)} N_2 and H_2+N_2 annealing. Arai's FT-IR also suggest this difference. It is well known that two peak spectra, 3d and LMM auger, have been mainly observed for arsenic compounds at XPS analysis. Figure 4 and 5 show As 3d and auger peak spectra for AsSG. respectively. In initial spectra for as deposited film, the binding energy of 3d peak is 45.leV and the kinetic energy of auger peak is 1217.4eV respectively, which correspond to the values for arsenic-oxides.



Fig.2 As profiles in $SiO_2/AsSG/SiO_2$ stacked films, before and after 16 hour annealing at $1000^{\circ}C$ in N₂ or H₂+N₂.



Fig.3 Arrhenius plots for determined As diffusivities in SiO₂ for N₂ and H₂+N₂ ambient.

After annealing in N_2 , the peak energies are still not changed. Thus, As atoms occupy the Si site and are bound with three O atoms in the SiO₂ network (the oxidized state).

After annealing in H2+N2, however, the 3d peak and the auger peak have shifted to 41.5eV and 1222.7eV, respectively. The binding energy value for the 3d peak is very close to that for metal As or SiAs, but slightly shifted to the high energy side. For auger peak spectra, the differences in kinetic energy value from that for metal As or SiAs (1225.5eV) are more obvious. Thus, it suggests that As-O bonds are almost broken. But As atoms are not completely bound with Si As atoms, such as exist in metal As or or SiAs. Therefore, As atoms are assumed to be out from the SiO2 network and exist pushed in interstitial sites (the reduced state).

From SIMS and XPS data, it results that the oxidized state As diffuse fast and the reduced state As diffused slow in SiO₂. The large activation energy value for N₂ may correspond to the bond breaking energy of SiO₂ network. Thus, the oxidized As change with Si atoms substitutionally with bond breaking of th network. On the other hand, the small activation energy for H_2+N_2 suggests the interstitial diffusion mechanism, and doesn't conflict with XPS data. The small diffusivity values may be caused by an inactivation of diffusion sites (unbounded oxygen) by H_2 termination from the analogy of Na diffusion in SiO₂.

The As chemical state transition is а reversible reaction. Figure 6 shows As profile change with sequential changes in annealing After ambient. first H2+N2 annealing, surface concentration was low and diffusion depth was shallow. However, after the next short time annealing in O_2+N_2 , gets surface concentration higher and subsequent N2 annealing has recovered the



52.0 50.0 48.0 46.0 44.0 42.0 40.0 38.0 36.0 34.0 32.0

Binding Energy eV

Fig.4 XPS As 3d peak spectra for AsSG films before and after annealing in N_2 or H_2+N_2 .



Fig.5 XPS As auger peak spectra for AsSG films before and after annealing in N_2 or H_2+N_2 .



Fig.6 As profile change in Si with sequential change of annealing ambients $(H_2+N_2 \rightarrow 0_2+N_2 \rightarrow N_2)$. An broken line is a N_2 annealing profile for reference.

surface concentration as same as that of N_2 annealing sample. These results correspond to As chemical state in SiO₂ had changed from the reduced state to the oxidized state again.

The As chemical state transition could be explained thermodynamically. Figure 7 shows standard formation energy - temperature diagram for SiO2 and As203. 02 concentration (partial pressure) values less than 10⁻¹⁰atm to reduce As^20^3 . In our required is 10ppm 02 experiments, about had been included in N2 gas as a contamination. Using the values of 02 diffusivity in SiO2 and oxidizing rate constant of 1 atm 02 ambient, in SiO₂ could 02 concentration be extrapolated to 1x10⁻⁷atm and was too high to reduced As203. For 10 percent H2+N2, however, H_2/H_2O ratio is about 10^4 and it is sufficient to reduce As_2O_3 (>10⁻²).

4. CONCLUSION

As diffusion in SiO₂ had The been using AsSG film. As investigated by diffusivities and chemical states in SiO₂ were different for N2 and H2+N2 annealing ambient. For N_2 , the chemical state was not changed from that of as deposited film, and it was the oxidized state with a large On the contrary, As had been diffusivity. changed to the reduced state with a small



Fig.7 Standard formation energy - temperature diagram of SiO₂ and As₂O₃.

diffusivity by H_2+N_2 annealing. The As diffusion mechanism was assumed as follows, the oxidized state As change with Si atoms substitutionally with a bond breaking of the SiO₂ network, and the reduced state As diffuses interstitially. The As chemical state transition was reversible and could be explained thermodynamically.

ACKNOWLEDGMENT

The authors wish to thank Prof. Α. Kunioka (Aoyama-Gakuin University) and Mr. Y. Amemiya (NTT) for a sample presentation of They also wish to thank Mr. SiAs crystals. (TOSHIBA) м. Kashiwaqi for useful discussions and encouragement. REFERENCES 1) K.Yamada, et al.; IEDM Tech.Dig.(1985) 702. 2) F.S.Becker, et al.; J. Electrochem. Soc. 136 (1989) 3033. 3) Y.Tsunashima, et al.; Ext. Abs. 21st SSDM, (1989) 181. 4) M.Gezzo, et al.; J. Electrochem. Soc. 120, (1973) 146. 5) K.Tsukamoto, et al.; Appl. Phys. Lett. 32, (1978) 117 6) Y.Wada, et al.; J. Electrochem. Soc. 128, (1981) 1317. 7) R.Singh, et al.; J. Electrochem. Soc. 131, (1984) 2645. 8) A.H.van Ommen; J.Appl.Phys.56 (1984) 2708. 9) T.Yamaji, et al.; J.Appl.Phys. 64 (1988) 2364. 10) S.T.Lee, et al.; Appl. Phys. Lett. 53 (1988) 189. 11) E.Arai, et al.; Jap.J.Appl.Phys. 9 (1970) 691.