Extended Abstracts of the 21st Conference on Solid State Devices and Materials, Tokyo, 1989, pp. 181-184

B-2-6

Chemical State and Diffusion Behavior of As in Arsenosilicate Glass (AsSG)

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Arsenic diffusion from Arsenosilicate glass (AsSG) is studied to realize a fine controlled doping process for the trench capacitor of 4Mbit DRAM. The chemical state of As in AsSG film is single, and it has large diffusivity. Therefore As diffusion is simple and fast in AsSG. In a high concentration film, the As precipitation occurs at the AsSG/Si interface during the diffusion annealing step, and precipitates function as a diffusion barrier for As into silicon. The precipitation is explained by the model based on the supersaturation of As in AsSG. The AsSG doping process become precise to control by suppressing the As precipitation at the interface.

INTRODUCTION

An high density DRAM of more than 4Mbits requires a three-dimensional structure such as a trench or stacked capacitor cell to reduce the storage capacitor area. To realize a trench capacitor with half Vcc operation, impurity doping into the trench sidewall is essential process to maintain storage capacitance with high soft error immunity. Using the conventional ion implantation technique, great differences occur in dopant concentration and junction depth between the sidewall and bottom of trenches. To overcome this problem, several other doping methods have been tested. Among them, solid phase diffusion from LPCVD arsenic doped SiO_2 (AsSG; Arsenosilicate Glass) films is one of the most promising technologies [1). Using this method, a conformable diffusion layer can be formed easily at narrow and deep trenches. Precise control, however, must be required for the dopant concentration and its profile.

In this paper, the diffusion behavior of arsenic (As) in AsSG/Si structure is investigated and related with chemical states of As in AsSG. One of limiting factors of the controllability, As precipitation at the interface was also investigated and explained with the supersaturation model of AsSG. A high controllability of the AsSG diffusion process is verified.

EXPERIMENTAL

AsSG films were prepared on (100) p-type Si wafers by a low pressure CVD technique using simultaneous thermal decomposion of TEOS (Tetra-EthOxy-Silane) and TEOA (Tri-EthOxy-Arsine) in a standard hotwall-type reactor. The typical film thickness was 100 nm, and its As concentration was varied from $1.3x10^{20}$ atoms/cm^3 to $1.4x10^{21}$ atoms/cm^3. Then the diffusion annealing processes were carried out in a nitrogen ambient at 1000C.

The diffusion experiments of implanted As in thermally grown SiO_2 were performed in order to compare with AsSG.

The As distributions were analyzed with Secondary Ion Mass Spectrometry (SIMS). In addition, Rutherford Backscattering Spectrometry (RBS) was also used to confirm

SIMS data of the interface region. The chemical states of As in SiO_2 were investigated by X-ray induced Photoelectron Spectroscopy (XPS).

RESULTS AND DISCUSSION

Fig.1. shows the As typical diffusion profiles of an AsSG/Si structure for different As concentration films after isothermally annealing at 1000C in N_2. Initial As concentrations of as deposited AsSG films are (a) $2x10^{20}$ and (b) $1x10^{21}$ atoms/cm^3 respectively. In the AsSG bulk region, diffusion profiles are simple and much the same in both cases. As concentration monotonously decreases toward the AsSG/Si interface.

But the difference occurs at the interface and silicon substrate. For low concentration films (a), As atoms diffuse from AsSG into Si substrate gradually. Thus As concentration is decreasing in AsSG and increasing in Si nearby the AsSG/Si interface with increasing annealing time. On the contrary, for high concentration films (b), As atoms not only diffuse into Si substrate but also start to accumulate in AsSG at the interface within an early stage of annealing. Once the accumulation layer has been formed, the supply of As diffusing into Si substrate was suppressed. Then in Si, As concentration decreases nearby the interface with increasing annealing time. Also from a direct observation of the interface, numerous precipitates, which correspond to the accumulated As, were seen in after annealing samples.

Fig.2. shows XPS As 3d peak spectra of high concentration AsSG film. In the case of as-deposited film (a), the binding energy of the peak is 45.1eV, which is close to the energy of As trioxides. Thus it suggests that in the as-deposited films, As atoms occupy the Si site and are bound with three O atoms in the SiO_2 network. Then the film had been annealed at 1000C in N_2 for 4 hours. No change could be observed at the peak in the bulk region (b). On the other hand, in the region nearby the interface (c), the peak has shifted at 41.2eV . This peak corresponds to the chemical state of accumulated As at the interface. The binding energy of the peak, 41.2eV, is the same as that of metal As or SiAs. Thus it suggests that As atoms are probably bound with Si atoms in the form of silicon-arsenide.

Fig.3 shows XPS spectra of implanted As in thermally grown SiO_2 to compare with AsSG. As 3d spectra has two peaks both in as implanted sample (a) and in after annealing

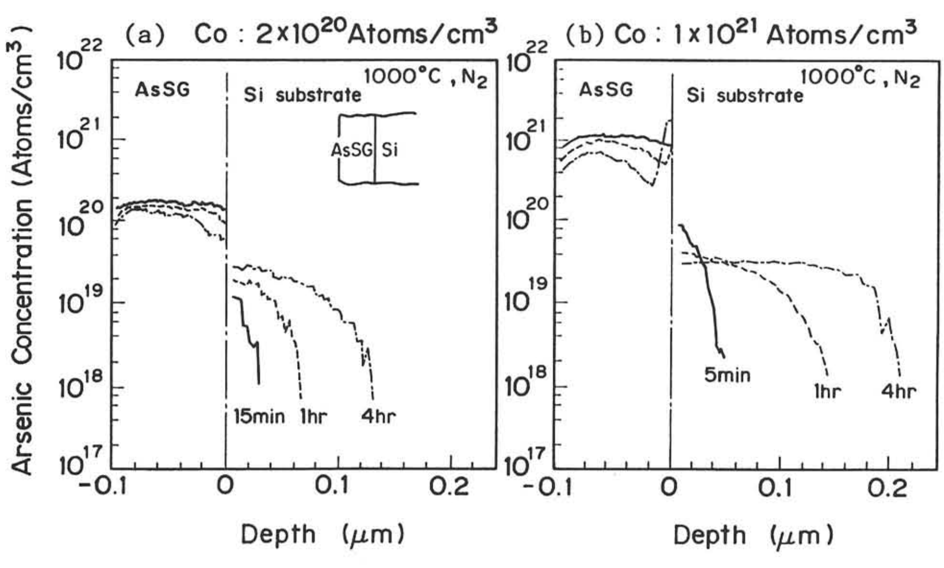

Fig.1 As diffusion profiles in AsSG/Si structure of the films with different initial concentrations during isothermal annealing at 1000C.

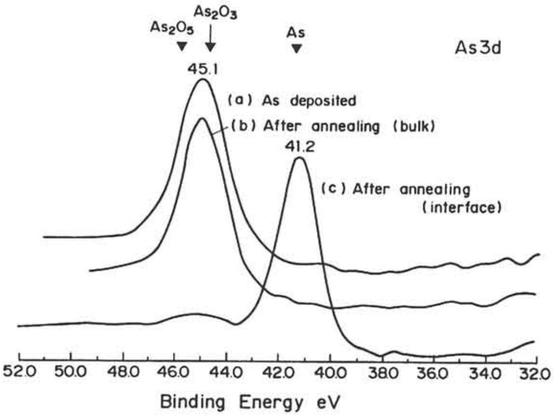

Fig.2 XPS As 3d peak spectra of AsSG films.

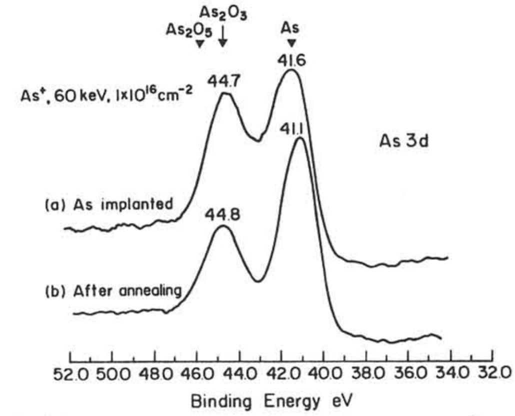

Fig.3 XPS As 3d peak spectra of implanted As in thermally grown SiO_2 films.

sample (b). The binding energy of these peaks are close to these of oxides and metal As respectively. Thus in the case of ion implantation, As atoms occupy both Si sites and O sites of the SiO_2.

Recently, diffusion behavior of implanted As in SiO_2 has been studied by many investigators [2)-7)]. It was found that As diffusion is very complicated. In particular, As become immobile at high concentration region for annealing in nonoxidation ambient. Our results of As diffusion in AsSG are different from these implantation data. The XPS data suggest that the difference of diffusion properties has come from the difference of chemical states of As. The diffusivities of As are presumed large for As atoms in Si sites and very little for As atoms in O sites. In the bulk region of AsSG, As atoms are only the single chemical state with large diffusivity. Thus As diffusion in AsSG is simple and easy to control except the precipitation at the interface.

The As precipitation phenomenon at AsSG/Si interface has been reported by several workers at about one decade previously [8)-11)]. But the precipitaion mechanism has not explained in detail. To explain the As precipitation, a new model are proposed. In this model, we consider that the As solubility in AsSG is not so high and estimated at 2×10^{20} atoms/cm^{-3} for 1000C. And higher than this concentration, As had been already supersaturated in AsSG at the deposition step. During the following annealing step, excessive As precipitates at the nucleation sites on the AsSG/Si interface. Because of the absence of nucleation sites in the bulk region, the precipitation is limited to the interface. Once the uniform precipitation layer has been formed at the interface, it becomes a perfect diffusion barrier for As. Then, only two fluxes have to be taken into account in order to derive the As distribution. They are the diffusion flux in AsSG; F1, and the precipitation flux from AsSG to the precipitation layer at the interface; F2.

$$F1=D_{AsSG}(\partial C/\partial x) \quad (1)$$

$$F2=k(C-C_e) \quad (2)$$

where D_{AsSG}: the As diffusivity in AsSG, k: the reaction rate constant of As precipitation, C_o: the initial As concentration of AsSG, C_e: the As concentration of AsSG equilibrate with precipitation layer (As solubility of AsSG).

For the structure of AsSG film sandwiched with uniform precipitation layers, the solution of diffusion equation can be described as follows

$$C=C_e+C_o\sum_{n=0}^{\infty}2\frac{\sin\delta n}{\delta n+\sin\delta n\cos\delta n}\times\exp(-\delta n^2D_{AsSG}t/X^2)\cos\delta n(x/X) \quad (3)$$

where δn is the value which satisfied

$$\cot\delta n=\delta n(k/D_{AsSG})X$$

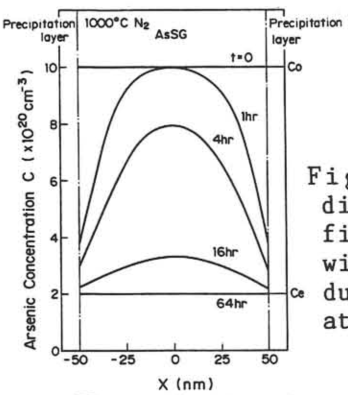

Fig.4 Calculation of As diffusion profiles in AsSG film, which was sandwiched with precipitation layers, during isothermal annealing at 1000C.

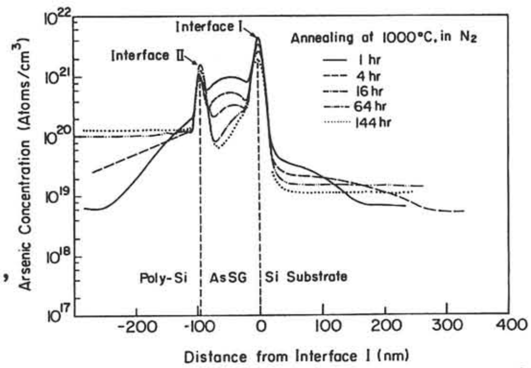

Fig.5 As diffusion profiles in the Si/AsSG/Si structure at 1000C.

The calculated results of isothermal annealing at 1000C are shown in Fig.4. Paying attention to the interface, the As concentration in AsSG is decreasing quickly at first,and approaching the As solubility with increasing annealing time. After 64 hours, the system reached an equilibrium state and remained unchanged during further annealing.

To confirm the calculation by the model, isothermal diffusion experiments of the poly-crystalline Si / AsSG / Si substrate, were carried out. Fig.5 shows overall diffusion profiles of this structure. Within 16 hours annealing, the profiles in AsSG agree well with the calculation results described above. To focus attention to Interface I the As concentration in AsSG is first decreasing, then pinning at about 2×10^{20} atoms/cm^3, the value which we estimated for As solubility. Also in Si, As concentration is decreasing with increasing annealing time, thus the precipitation layer functions as a diffusion barrier for As. These results are consistent with the calculation results based on the supersaturation model.

On the contrary, at the Interface II, the pinning of the As concentration cannot be observed in AsSG and As concentration is not decreasing in the poly-Si region. Thus the precipitation at Interface 2 is not a uniform layer, and it will be caused by the fast diffusion through the poly-Si grain boundary or the interface roughness. Therefore the results of Interface II will not hinder the confirmation of the model.

From the model, it is confirmed that As precipitation is the intrinsic phenomenon of As-Si-O system. Thus AsSG film is set an optimum concentration, As precipitation is suppressed, and precise control can be achieved for its diffusion profile.

CONCLUSION

The As diffusion in AsSG/Si structure was investigated. The chemical state of As in AsSG is a single state with Large diffusivity, therefore As diffuses simple and fast in AsSG. In high concentration films, As precipitation occurs at AsSG/Si interface and functions as a diffusion barrier for As. The precipitation is explained by the supersaturation model. In result, the AsSG diffusion process become precise to adopt it for the trench doping of Mbit DRAMs.

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