Rapid Thermal Diffusion of Sn from Spin-on-Glass into GaAs

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ABSTRACT

Diffusion of dopants into semiconductors from a spin-on-glass (SOG) source is of great interest because of its versatility, simplicity, and relatively low cost. SiO_2 SOG films doped with Sn and/or Ga were used as a diffusion source on GaAs. Diffusion was studied during rapid thermal annealing with or without an As over-pressure ambient, which was produced by either the proximity over-pressure or the enhanced over-pressure proximity techniques. Diffusivity of Sn was observed to decrease as As over-pressure increases. Modifying the Sn doped SOG to contain 4 mole percent Ga slightly reduced the Sn diffusivity. An explanation of these results is proposed based on the chemical reactions between the SOG and GaAs. Highly doped layers (1-3 $\times$ 10^{18} cm^{-3}) with good electron mobility (>1000 $cm^2/V \cdot s$) resulting in abrupt shallow junctions (<0.5 μm) were obtained.

Introduction

Spin-on-glass (SOG) films have many applications in integrated circuit fabrication. For example, they can be used as a dielectric material, a planarizing agent, or a diffusion source.[1,2] Good quality oxides have been obtained by SOG films with the appropriate annealing processes.[3a,b] Deposition of SOG films can be accomplished without the use of vacuum equipment resulting in a relatively simple and low cost technique. Although, ion implantation is well characterized and can be used to introduce impurities at a concentration level higher than their solubility limit, it requires the use of expensive equipment and may severely modify the material being implanted due to the physical interaction of the implanted ions and the solid *(i.e.,* sputtering, crystal damage).

SOG films can be prepared with precise amounts of dopants, and their intimate contact with the material to be doped contributes to a consistent doping process. Further control of the doping process is realized through annealing. The use of rapid thermal processing (RTP) results in a low thermal budget and shallow junction depths. The ambient during annealing, also effects dopant diffusion. Although plasma-enhanced chemical vapor deposition (PECVD) silicon oxide films are considered capping layers against incongruent As losses from the GaAs surface,[4] SOG films are usually less dense than PECVD films and may allow an As over-pressure ambient to influence the diffusion from an SOG overlayer.

The diffusion of Sn from SOG films into GaAs has been reported previously using conventional furnace annealing.[2] In this paper, a study of Sn diffusion from SOG films into GaAs using RTP as presented. The influence of an As over-pressure ambient on Sn diffusion from SOG into GaAs is studied for the first time. The effect of SOG film dopant content on the diffusion process is also analyzed.

Experimental

The undoped SOG source was prepared at room temperature from ethanol, tetraethoxysilane (TEOS), water, and hydrochloric acid using a method that has been described elsewhere.[5] Tin isopropoxide [$Sn(OC_3H_7)_4$], and gallium nitrate hydrate [$Ga(NO_3)_3 \cdot xH_2O$] were introduced into the SOG to provide Sn and Ga doping, as required. SOG sources with 5 and 10 mole percent (m/o) Sn were prepared by modifying the undoped source chemistry. In addition, an SOG source was created that contained both 5 m/o Sn, and 4 m/o Ga.

Films were deposited by spin-casting the SOG onto undoped semi-insulating (100) GaAs substrates at 3000 rpm. After curing, film thickness were approximately 130 nm. The curing was performed on a hot plate followed by a furnace anneal in the following sequence:

1. 90°C/90 s—hot plate, room ambient
2. 160°C/90 s—hot plate, room ambient
3. 260°C/90s—hot plate, room ambient
4. 430°C/30 min—furnace, N_2 ambient

The hot plate temperature was ramped between steps 1 to 2 and 2 to 3, with the sample on the hot plate. Between steps 3 and 4, however, the sample was allowed to cool to room temperature.

After film deposition and curing, the drive-in diffusion was performed by means of RTP using an AG Heat Pulse 410 system. The sample to be heated was placed on a silicon wafer with a thermocouple embedded in the Si wafer. The processing temperature was varied from 850 to 1000°C, and annealing time was fixed at 60 s. Samples were annealed in a nitrogen atmosphere, and heated at a rate of 50°C/s.

The ambient during annealing was also varied. One of three annealing conditions was used: (*i*) no As over-pressure (NOP), (*ii*) proximity As over-pressure (POP) using a GaAs wafer on top of the sample, and (*iii*) enhanced over-pressure proximity (EOP)[6] using a GaAs wafer with an SnGaAs surface layer in proximity to the sample. It has been shown that the EOP method creates a higher As over-pressure ambient than the POP method.[6]

After RTP, the SOG films were visually inspected and removed by an aqueous solution of hydrofluoric acid. Energy dispersive spectroscopy (EDS) measurements were taken using a Kevex 3203 detector attached to a JOEL 733 electron microprobe. The sheet resistance, R_S, carrier concentration, N_S, and carrier mobility, μ_n, of the diffused layers were characterized by Hall effect measurements. Electrochemical capacitance-voltage (C-V) profiles were measured with a Polaron (made by Bio-Rad, Inc.) system. The C-V data was used to determine the electrically active dopant concentration. Secondary ion mass spectroscopy (SIMS) was measured with an MIQ-256 Cameca-Riber

Table I. Hall effect measurements: sheet carrier concentration, sheet resistance and electron mobility, of GaAs samples with Sn diffusion from SOG films with 5 and 10% Sn, annealed by RTP at varying temperature for 60 s and with no As over-pressure.

% of Sn in SOG	T [°C]	N_S ($10^{13}/cm^2$)	R_S (Ω/□)	($cm^2/V \cdot s$)
5	850	2.98	205	1020
10	850	3.72	159	1060
5	900	4.90	110	1160
10	900	6.07	96	1080
5	950	8.62	64	1130
10	950	10.2	59	1040
5	1000	12.6	44	1120
10	1000	16.9	36	1030

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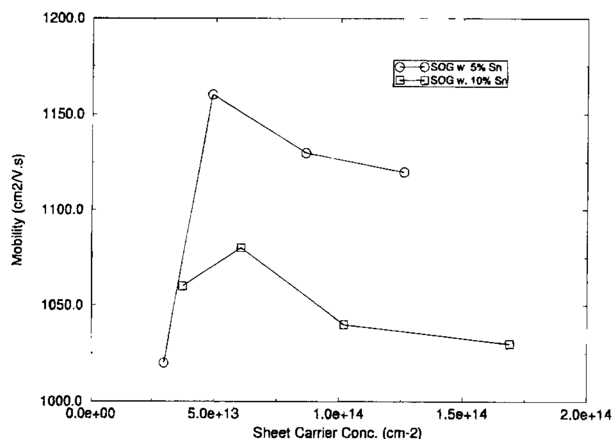


Fig. 1. Electron mobility *vs.* sheet carrier concentration of samples with Sn diffused from SOG films with 5 or 10% Sn.

system and was used to determine the atomic concentration profile.

Results and Discussion

Small dots and microcracks were observed on some SOG samples with 10 and 5% Sn + 4% Ga, after annealing. Examination of the defects by EDS showed that the dots were Sn and/or Ga rich. The microcracks were seen to originate mainly from the small dots.

Hall effect measurements are shown in Tables I to IV. Table I presents the results of the samples annealed under NOP conditions. Sheet carrier concentration increased as both the RTP temperature and the amount of Sn in the film increased. As depicted in Fig. 1, the electron mobility for the 10% Sn films was lower than that of the 5% Sn films. The following discussion refers to films containing 5% Sn.

Tables II-IV show the doped layer average carrier concentration, sheet resistance, and electron mobility, respectively, for samples annealed under different As over-pressure ambient and with or without the addition of Ga to the SOG. The carrier concentration increases with increasing RTP temperature and decreases with increasing As over-pressure. The addition of Ga also reduces the sheet carrier concentration, however, to a smaller degree than varying the As over-pressure.

Electrically active dopant concentration profiles measured by electrochemical C-V are shown in Fig. 2 and 3. Figure 2 demonstrates that increasing As over-pressure reduces the junction depth and the maximum carrier concentration. Figure 3 shows the effect of adding Ga to the film. A slight reduction in the diffusion layer thickness was observed.

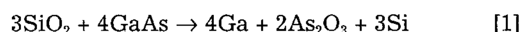
The atomic concentration profiles obtained by SIMS for samples made from SOG films containing 5% Sn or 5% Sn + 4% Ga, and annealed at 900°C at varying As over-pressure ambient are shown in Fig. 4. These profiles are similar to the ones shown in Fig. 2b and 3. They confirm the enhanced diffusion for NOP conditions compared to those under EOP conditions. An intermediate diffusion rate was observed for samples created from NOP anneals of SOG films containing 5% Sn + 4% Ga.

Taking the activation level as the ratio between the C-V and SIMS profiles, an activation level of 80% for the sample prepared under EOP condition is calculated. The sample prepared using the NOP conditions had a 70% activation level. Similar dependence of diffusion profiles of Zn on the As over-pressure ambient has also recently been observed.[7]

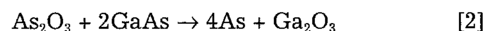
Table III. Sheet resistance (Ω/□) of diffusions at different As over-pressure ambient and temperatures for 60 s for SOG films with fixed Sn and optional Ga content.

% of Sn	% of Ga	As ambient	850°C	900°C	950°C	1000°C
5	—	NOP	205	110	64	44
5	—	POP	294	169	78	46
5	—	EOP	713	356	125	85
5	4	NOP	265	136	127	54

Katayama *et al.*[4] proposed a model which can account for these observations. During annealing, free Ga and As atoms are produced at the SiO_2/GaAs interface



$$3SiO_2 + 4GaAs \rightarrow 4Ga + 2As_2O_3 + 3Si \quad [1]$$



$$As_2O_3 + 2GaAs \rightarrow 4As + Ga_2O_3 \quad [2]$$

The free Ga atoms penetrate the SiO_2 film and diffuse rapidly at the annealing temperature.[8] In addition, some of the free Ga atoms diffuse interstitially into the GaAs. Interstitial Ga was known to produce the "kick-out" effect,[9] and can kick-out substitutional Sn on a Ga lattice site. Sn may now diffuse interstitially, with a smaller activation energy, resulting in enhanced diffusion. The free As atoms can cause emission of Ga vacancies from the interface into the GaAs lattice. Ga vacancies promote the substitutional-interstitial dissociation (SID) mechanism,[10] producing substitutional Sn and consequently an increase of the solubility of Sn.

As a result of these interfacial reactions, Ga interstitials and vacancies will exist above their thermal equilibrium concentrations, and the diffusivity and solubility of dopants like Sn will increase in the GaAs near this interface. An increase of As interstitials and vacancies is also possible, however, these do not directly affect the diffusivity and solubility of Sn.

With no As over-pressure ambient, arsenic evaporates from the interface through the SOG film which may possess a high density of micropores.[11] Additional film integrity may be lost since the SOG film is subject to a tensile stress during heating due to the lower thermal expansion coefficient of SiO_2 compared to GaAs and to a temperature gradient between SOG film and the substrate.[13] Consequently, with no As over-pressure, As losses will occur and the interfacial reactions will proceed, enhancing the Sn in-diffusion. With increasing As over-pressure ambient, the interface reactions will slow and consequently reduce the Sn in-diffusion (Tables II to IV and Fig. 2 and 4).

By adding Ga to the SOG film, a similar reduction of the interface reactions occurs due to Ga accumulation at the interface, which results in a reduction of the Sn in-diffusion. It should be noted that the above results (Tables II to IV and Fig. 3) indicate that the influence of adding 4% Ga to the SOG film was less pronounced than the influence of the As over-pressure ambient.

The Boltzmann-Matano technique was used to extract the diffusivity of Sn from the measured concentration profiles.[13] Figure 5 presents Sn diffusion coefficients at a doping level of $10^{18}/cm^3$ *vs.* the inverse absolute temperature for SOG films containing 5% Sn at three different As over-

Table II. Sheet carrier concentration ($\times 10^{13}/cm^2$) of diffusions at different As over-pressure ambient and temperatures for 60 s for SOG films with fixed Sn and optional Ga content.

% of Sn	% of Ga	As ambient	850°C	900°C	950°C	1000°C
5	—	NOP	2.98	4.90	8.62	12.6
5	—	POP	1.70	2.93	8.17	12.0
5	—	EOP	0.95	1.40	3.79	5.32
5	4	NOP	2.70	4.24	6.76	10.8

Table IV. Electron mobility ($cm^2/V \cdot s$) of diffusions at different As over-pressure ambient and temperatures for 60 s for SOG films with fixed Sn and optional Ga content.

% of Sn	% of Ga	As ambient	850°C	900°C	950°C	1000°C
5	—	NOP	1020	1160	1130	1120
5	—	POP	1250	1260	978	1140
5	—	EOP	926	1260	1320	1380
5	4	NOP	875	1090	730	1080

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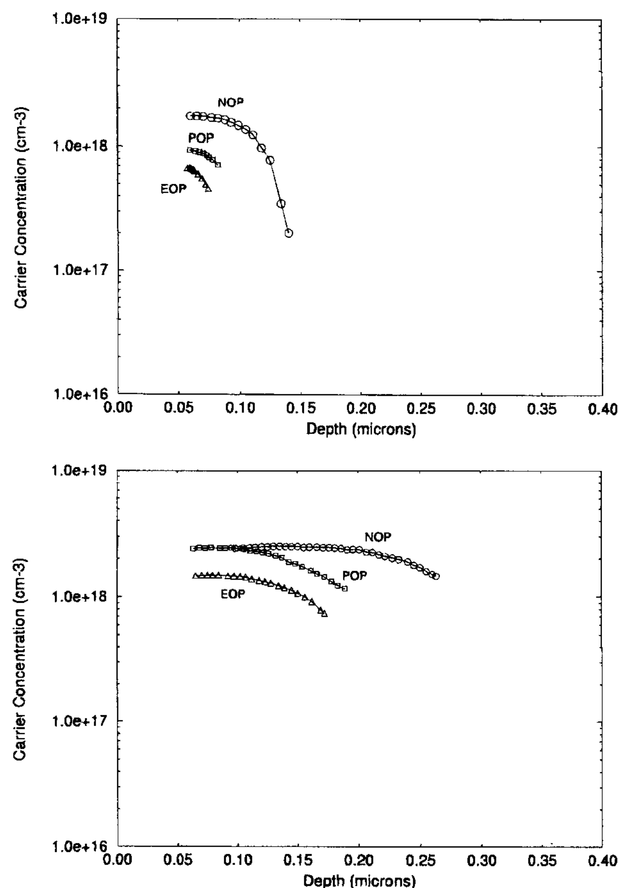

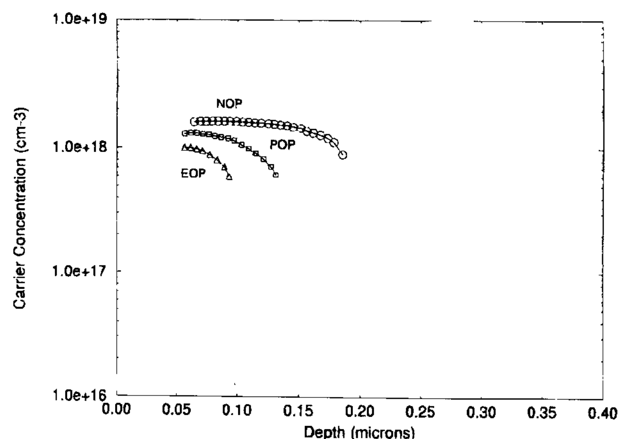

Fig. 2. Carrier concentration profile obtained by electrochemical C-V of samples with 5% Sn SOG films annealed for 60 s at different As over-pressure ambient at (a, top left) 850, (b, above) 900, and (c, left) 950°C.

pressure conditions. From this data, activation energies of 2.3 and 3.2 eV were obtained for the NOP and EOP conditions, respectively, indicating a difference in diffusion mechanisms.

With no As over-pressure (NOP), an activation energy of 2.3 eV is consistent with a predominant interstitial diffusion mechanism,[2] as performed through the SID[10] and kick-out[9] processes. This mechanism is expected to dominate if the proposed increase in Ga vacancies and interstitials due to NOP is correct. Under EOP conditions, an activation energy of 3.2 eV is obtained, indicating that the Sn diffusivity is dominated by substitutional diffusion through Ga sites.[2] A substitutional diffusion mechanism is expected to dominate if no excess Ga vacancies and/or interstitials are emitted into the interface region of the GaAs. The observed difference in activation energies for the NOP and EOP conditions supports Katayama's model.[4]

POP annealing conditions produce intermediate diffusion coefficients with an apparent activation energy of 3.9 eV. This value indicates that the dominant diffusion mechanism changes during processing. At low temperatures, the POP method was as effective as the EOP method in suppressing the As evaporation and substitutional diffusion dominates. However, at high temperatures, the As over-pressure produced by the proximity method was not successful in suppressing the As evaporation. Consequently, annealing conditions approach NOP conditions where diffusion is predominantly interstitial.

Conclusions

It has been shown that the rapid thermal processing of doped SOG films can be used as a diffusion source for

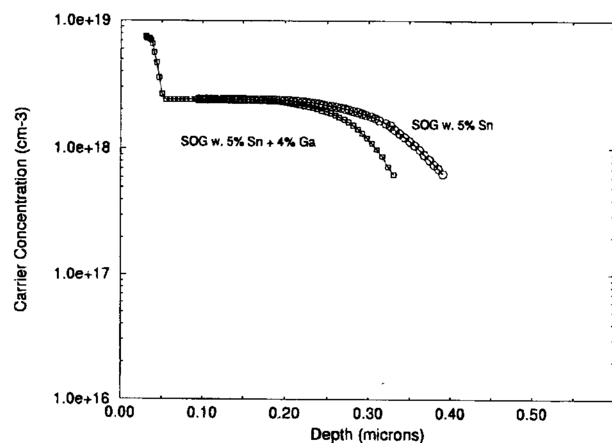

Fig. 3. Carrier concentration profiles obtained by electrochemical C-V of samples with 5% Sn SOG films or 5% Sn + 4% Ga SOG films annealed at 1000°C for 60 s.

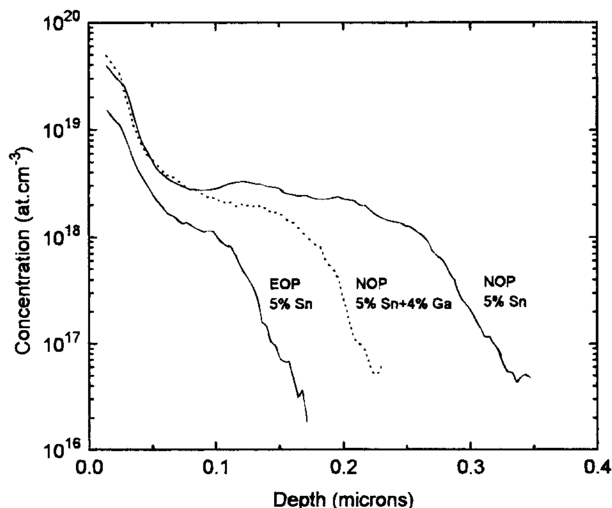

Fig. 4. Atomic concentration profiles obtained by SIMS of samples with 5% Sn SOG films or with 5% Sn + 4% Ga SOG films, annealed at 900°C for 60 s at different As over-pressure ambient.

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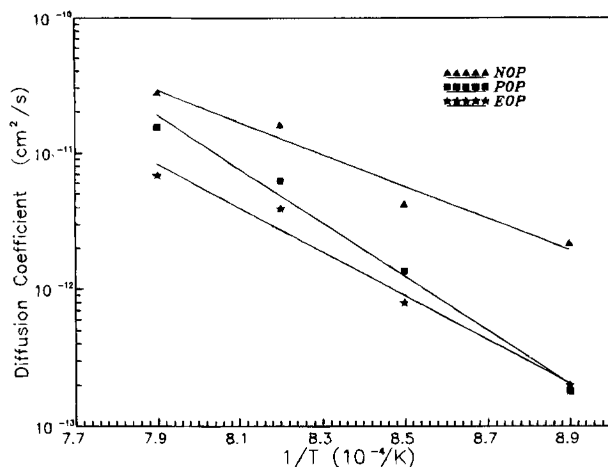

Fig. 5. Arrhenius plot of the diffusion coefficients obtained under different As over-pressure ambient for samples with 5% Sn SOG films and annealed for 60 s.

GaAs. Sn diffusion layers in GaAs were obtained with carrier concentrations in the range of 1 to 3 $\times 10^{18}$ cm^{-3}, and mobilities higher than 1000 cm^2/V · s. The results are similar to those obtained by conventional furnace annealing.[2] However, the use of RTP produces abrupt and shallow junctions ($X_j < 0.5$ μm) due to the short time involved.

It was shown that diffusivity of Sn from SOG films using RTP depends on the As over-pressure conditions. The higher the As over-pressure during the RTP treatment, the lower the diffusivity of Sn in GaAs. This was explained by applying Katayama's model[4] where emission of point defects due to the interface reactions between SiO_2 and GaAs increases the diffusivity of Sn. These reactions and the emission of point defects were reduced by increasing the As over-pressure and/or adding Ga to the SOG film.

Samples annealed without an As over-pressure showed an Sn diffusivity activation energy of 2.3 eV. This indicates that the Sn atoms are diffusing predominately by an interstitial mechanism. A dopant activation level of 70% was measured on samples annealed without an As over-pressure. Annealing with an As over-pressure ambient reduces the Sn carrier concentration, relative to annealing without an As over-pressure. Samples annealed using the enhanced over-pressure proximity method (EOP) had an activation energy for tin diffusion of 3.2 eV, and a dopant activation level of 80%. The predominant diffusion mechanism was assumed to be substitutional.

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