DOPANT ACTIVATION IN POLY-$SI_{1-x}GE_x$ AT LOW TEMPERATURE

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Abstract -Isothermal annealing of boron or phosphorus implanted polycrystalline $Si_{1-x}Ge_x$ thin films, with x varying from 0.3 to 0.55 was reported in this paper. In low temperature (<=600°C) annealing, grain boundary segregation causes both the conductivity and the Hall mobility to decrease during extended annealing. The effective activation of phosphorus was less than 20% and decreases with increasing Ge content. Boron activation could reach above 70%. It was also found that $Si_{1-x}Ge_x$ could be oxidized at 600°C in a conventional furnace even with pure N_2 protection.

I. Introduction

Polycrystalline $Si_{1-x}Ge_x$ (poly-SiGe) is an attractive alternative to polycrystalline silicon (poly-Si) in silicon integrated circuits [1]. The advantages of poly-SiGe over poly-Si include low thermal budget and high mobility. For undoped $Si_{1-x}Ge_x$, crystallization can occur at a much lower temperature or for a shorter annealing time than for silicon [2]. Some authors[3,4] also pointed out that the boron activation in poly-SiGe was much easier than in poly-Si. The activation behavior of doped poly-SiGe as a function of the annealing conditions has been studied[4]. However, the explanations for some phenomena are still far from clear, such as why the resistivity of the phosphorus doped poly-$Si_{1-x}Ge_x$ increases rapidly with increasing x when x>0.5[4], how and why the Hall mobility and the carrier concentration depend on the Ge content. Furthermore, it is still not clear what temperature-time cycles are necessary to activate dopants in poly-SiGe, particularly for low temperature thin film transistors.

In this Paper, we present the results of a study on the low temperature annealing of implanted poly- $Si_{1-x}Ge_x$, with x varying from 0.3 to 0.55. Hall Effect measurements were used to measure the electrical characteristics of doped poly-SiGe. Powder X-ray diffraction (XRD) was used to characterize the crystal structure. X-ray photoelectron spectroscopy (XPS) was used to measure the film composition and the chemical bonding states of the elements.

II. Experimental

Poly-SiGe films were deposited at low pressure (0.3 Torr) by chemical vapor deposition at 450°C or 500°C on thermally oxidized (100), p-type, 100mm Si wafers. The source gases were SiH_4 and GeH_4. The deposition conditions and SiGe film thickness were shown in Table 1. To make sure the SiGe thin films were crystallized completely, all Samples were annealed at 550°C for 7 hours in N_2 immediately following the SiGe deposition.

Table 1. SiGe deposition conditions and results.

	Deposition temperature (°C)	SiH_4/GeH_4 flow rate (sccm)	Ge content (%)	SiGe thickness (nm)
1	450	70/22	55	250
2	500	70/10	30	200
3	450	70/10	45	210

Phosphorus or boron was implanted for two consecutive times to obtain a smooth concentration profile. For the p-type samples, boron was implanted at 35KeV and a dose of $2\times15cm^{-2}$, followed by BF_2 at 35KeV and a dose of $2\times10^{15}cm^{-2}$. For the n-type samples, phosphorus was implanted at 80KeV and a dose of $2\times10^{15}cm^{-2}$, followed by the same ion at 40KeV and a dose of $2\times10^{15}cm^{-2}$. All the implanted wafers were cut into $1\times1cm^2$ square pieces . Some of them were capped with 100nm LTO deposited at 425°C. The samples were annealed at different temperatures from 500°C to 600°C. Annealing time was from 30 seconds to 20 hours. The 30-second to 5-minute anneals were done in a rapid

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thermal annealing (RTA) reactor while the 15-minute to 20-hour anneals were done in a conventional furnace. All the anneals were done in a pure N_2 ambient.

After annealing, all the samples were measured in a Hall Effect measurement system to estimate the sheet resistance, the Hall mobility and the carrier concentration. Some of the samples were analyzed by powder XRD and XPS.

III. Results

The resistivity of the p-type and the n-type $Si_{0.45}Ge_{0.55}$ films as a function of the annealing time at different temperatures is summarized in Figure 1. The behavior is very similar between the n- and the p-type samples, though the resistivity of the n-type samples is always higher than that of the p-type samples. The resistivity of all the samples first decreases quickly with annealing time, then increases gradually upon further annealing. For the boron doped samples, resistivity as low as 3 mΩ-cm can be obtained after 5 minutes of annealing at 600°C. For the phosphorus doped samples, the lowest resistivity, about 30 mΩ-cm was obtained after 15 minutes of annealing at 600°C. The behavior of the samples with and without the LTO caps was similar for annealing time less than 6 hours at 600°C. Beyond 6 hours, the resistivity of the samples without the LTO caps increased more quickly than that of the samples with the LTO caps, especially for the n-type samples. After 12 hours of annealing at 600°C, the resistivity of the n-type samples without the LTO caps became too large to be measurable in the Hall Effect measurement system.

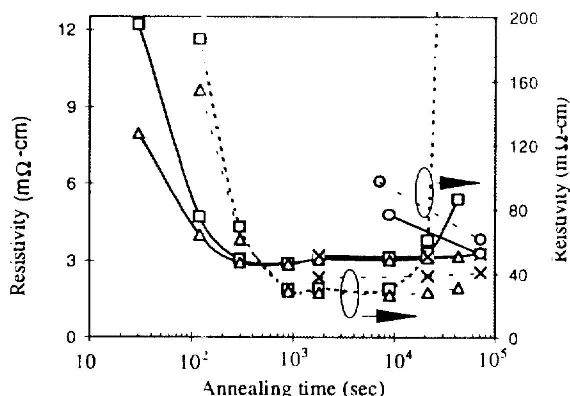

Fig.1 The Resistivity of the p-type (solid lines) and the n-type $Si_{0.45}Ge_{0.55}$ (dotted lines) as a function of annealing time at different temperature. Lines with squares are for samples annealed at 600°C without LTO cap. Lines with triangles are for samples annealed at 600°C with LTO caps. Lines with crosses are for samples annealed at 550°C and lines with circles are for those annealed at 500°C.

The Hall mobility and the effective dopant activation of the p-type and the n-type $Si_{0.45}Ge_{0.55}$ films as functions of annealing time at different temperatures are summarized in Figure 2. Comparing Figures 1 and 2, we can see that for the p-type samples, the decrease of the resistivity with annealing time during the first 5 minutes of annealing is due to both increases in the mobility and in the effective dopant activation. But for the n-type samples, the decrease in the resistivity is due mainly to the mobility increase during the first 15 minutes of annealing. Effective phosphorus activation decreases monotonically with the annealing time in all the experiments. After 5 minutes of annealing, both the conductivity and the effective dopant activation of the p-type samples decrease slowly with the annealing time. The reason for the decrease in effective dopant activation with annealing time is possibly grain boundary segregation[5] or formation of dopant pairs[6], or both. The behavior was similar for the samples with or without the LTO caps when the annealing time was less than 6 hours. But the effective dopant activation of the samples without the LTO caps decreases rapidly with annealing time beyond 6 hours. This phenomenon will be further elaborated on later in the Paper.

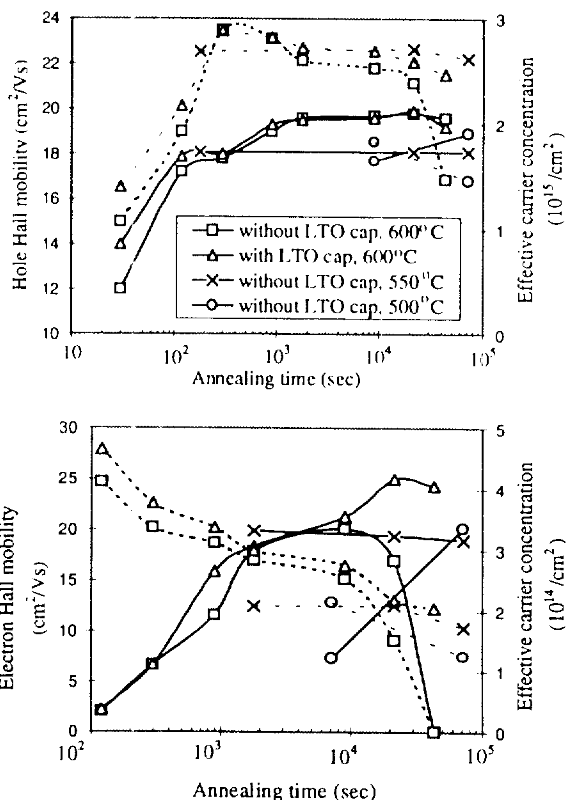

Fig.2 The Hall mobility (solid lines) and the dopant activation (dotted lines) of (a) the p-type (upper) and (b) the n-type type (bottom) $Si_{0.45}Ge_{0.55}$ as functions of annealing time.

The sheet resistance of the n-type $Si_{0.45}Ge_{0.55}$ after 30 seconds of annealing at 600°C was still out of the range of the Hall Effect measurement system while the p-type

samples had sheet resistance values of lower than 500Ω per square. This is because the implant damage by phosphorus at 80KeV is more severe than that of boron at 35KeV. From the XRD results shown in Figure 3, we can see that the crystallization is far from complete for the n-type $Si_{0.45}Ge_{0.55}$ when compared to the p-type samples. Crystallization was almost complete after just 30 seconds of annealing at 600°C for the p-type samples. But for the n-type samples, the time needed was more than 5 minutes. After 15 minutes of annealing at 600°C, the structures became stable for both the n-type and the p-type samples, as indicated by the XRD results.

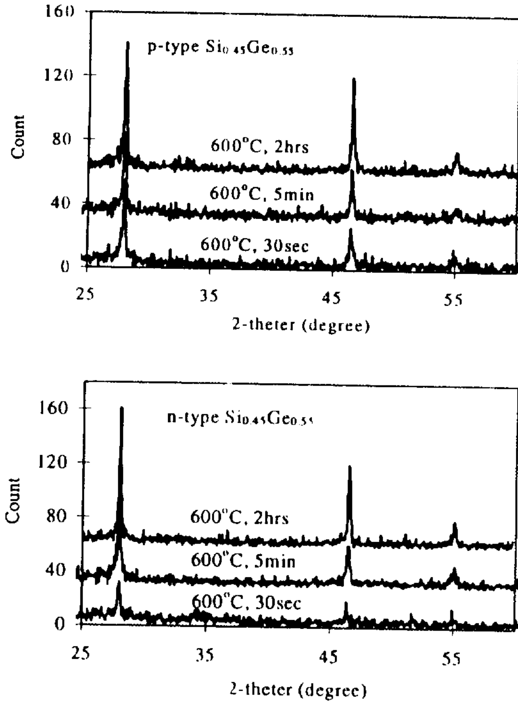

Fig.3 XRD results of the p-type (upper) and the n-type (bottom) $Si_{0.45}Ge_{0.55}$ after annealed for 30 seconds, 5 minutes, and 2 hours at 600°C.

In Figure 4, the different annealing behavior of the n-type samples with different Ge contents are compared. It can be seen that the conductivity, the Hall mobility and the effective dopant activation of the low Ge content samples were lower than those of the high Ge content samples. This is similar to the results obtained by King and co-workers[4]. But in their results, the resistivity increased much more rapidly with the Ge content than what we observed when the Ge content was above 50%. From our experiments, we also noticed that the necessary annealing time and temperature (Table 2) were much less for the high Ge content samples.

IV. Discussion

For the low Ge content SiGe films, Noguchi and co-workers[8] have shown that the resistivity was similar among samples with or without the LTO caps during the annealing. In our experiments, the resistivity of the high Ge content samples changed significantly between those with the LTO caps and those without the LTO caps especially for the phosphorus doped samples. From

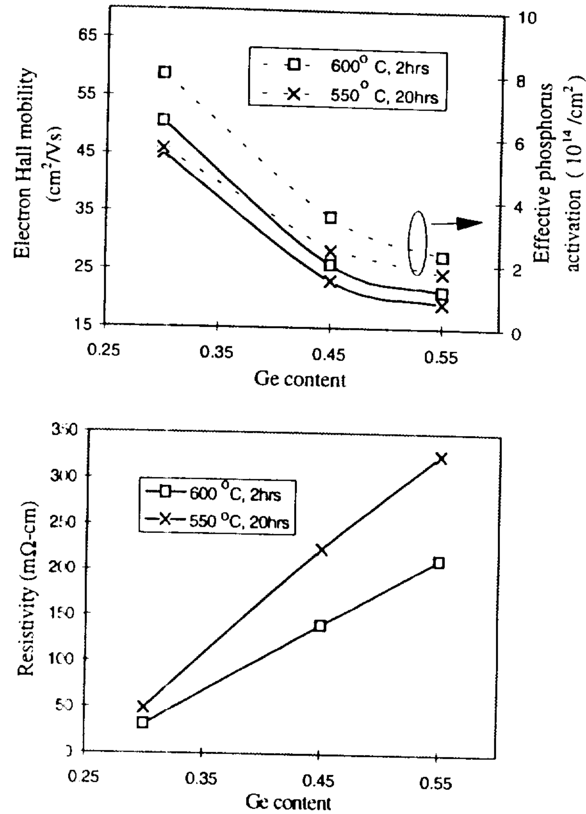

Fig.4 The resistivity, the hall mobility and the effective dopant activation of n-type poly-SiGe as functions of the germanium content at different annealing temperatures after the ion Implantation.

Table 2 Annealing time necessary in different temperature to obtain sheet resistance lower than 5KΩ. The final sheet resistance obtained after the annealing schedule is also shown.

	500°C	550°C	600°C
N-type $Si_{0.3}Ge_{0.7}$	> 20 hours > 1MΩ	20 hours 246Ω	30 minutes 179Ω
N-type $Si_{0.55}Ge_{0.45}$	>20 hours > 1MΩ	30 minutes 1.8KΩ	15 minutes 559Ω
N-type $Si_{0.45}Ge_{0.55}$	2 hours 3.9KΩ	30 minutes 1.5KΩ	5 minutes 2.45KΩ
P-type $Si_{0.45}Ge_{0.55}$	2 hours 128Ω	30 minutes 128Ω	30 seconds 318Ω

Figure 2, we can see that the carrier concentration and the conductivity decrease with long annealing time at 600°C for samples without the LTO caps. After 12 hours of annealing, the resistivity of the n-type samples without the LTO caps was out of the measurement range of the equipment. We suspect oxidization played an important role here. In a conventional furnace, it is difficult to

eliminate trace amount of oxygen even in a "pure" nitrogen ambient. SiGe can be oxidized at low temperature[9]. This oxidization could be enhanced by the implanted phosphorus[10]. XPS profile of $Si_{0.45}Ge_{0.55}$ without the LTO cap after 6 hours of annealing in a conventional furnace at 600°C with nitrogen protection clearly shows that the top 30nm was completely oxidized. It is also shown from the XPS results that Ge piles up at the interface between the oxide and the SiGe layers, similar to the thermal oxidation of SiGe [11].

For the LTO capped n-type samples, the resistivity still increases with the Ge content. This is because of the low effective activation of phosphorus and the low electron mobility in the samples with high Ge content, as shown in Figure 7. Herzer and Kalbitzer [7] showed that phosphorus activation in crystalline Ge is as low as 20 percent, which is much lower than in crystalline Si. The mobility in poly-crystalline material was dependent also on the carrier concentration [12]. Therefore the low activation of phosphorus in high Ge content poly-SiGe is also a reason for the low mobility. The reason for the low effective activation of phosphorus may be caused by the electronic states in the grain boundaries. It has been shown [13] that in poly-Ge grain boundaries, a partially filled band of electronic states exists near the valance band. This band would decrease the effective electron concentration and the electron mobility The characteristics of the high Ge content poly-SiGe should be similar to those of poly-Ge. Also, the Ge may enhance the grain boundary segregation of phosphorus. The un-activated phosphorus may exists as phosphorus clusters, especially in the grain boundaries. This will change the material structure and enhance the electron scattering. Hence the electron mobility decreases with increasing Ge content.

The boron activation and the hole mobility of high Ge content poly-SiGe were not bad compared with poly-Si. In our experiments, 70 percent effective activation can be obtained. Boron activation also decreased slowly with extended annealing. This maybe due to boron pairs formation [6] or grain boundary segregation. The hole mobility of high Ge content poly-SiGe can reach a value $20cm^2/Vs$. This could be due to the high boron activation and the smaller density of hole traps in the grain boundaries, contrary to the n-type[13] samples.

V. Conclusion

This study showed that dopant segregation may exist in both boron and phosphorus doped SiGe thin films. Dopant segregation causes the conductivity and the Hall mobility to decrease during extended annealing. Phosphorus activation and electron mobility decrease with increasing Ge content. One of the possible reasons is the change in the grain boundary trap density with Ge content. Poly-SiGe films, especially those with high Ge content, can be oxidized at low temperature in a conventional furnace even with "pure" nitrogen protection. This oxidization can be enhanced by heavy phosphorus doping. XPS results showed that Ge piled up at the interface when SiGe was oxidized.

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