第28卷　第3期　　半 导 体 学 报　　Vol.28　No.3
2007年3月　　CHINESE JOURNAL OF SEMICONDUCTORS　　Mar.,2007

Hydrogenation of Polycrystalline SiGe Thin Films by Hot Wire Technique*

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Abstract: An optimized condition for defect passivation by the hot-wire technique was established. Effects of hydrogenation for polycrystalline SiGe (poly-$Si_{1-x}Ge_x$) thin films were estimated by investigating the dark conductivity and activation energy that derive from the conductivity as a function of the temperature. The results show that this technique can effectively reduce defects present in poly-$Si_{1-x}Ge_x$ films. By optimizing the substrate and filament temperatures, the treatment can be accomplished in a short time of 20～30min, which is considerably shorter than other hydrogenation techniques.

Key words: hot-wire; hydrogenation; polycrystalline SiGe
PACC: 7360J; 6780M; 8140R
CLC number: TN304.055　　**Document code**: A　　**Article ID**: 0253-4177(2007)03-0317-06

1 Introduction

Polycrystalline Si (poly-Si) has been a key material in the fabrication processes for MOS-LSI in recent decades. Moreover, un-doped or highly doped poly-Si films have been required to realize high performance thin film transistors (TFTs) for flat panel displays. However, as-deposited polycrystalline silicon films with fine grains cannot be applied to the active devices because of a high density of defects at the grain boundaries. These defects reduce carrier diffusion lengths in poly-Si and destroy device performance. Hydrogen-passivation, or hydrogenation treatment, is a popular and effective technique to reduce the effective density of electrically active defects in poly-Si films[1～5]. A decrease of the effective trap density generally causes a decrease in the resistivity of the heavily doped poly-Si films. On the other hand, the hydrogenation treatment increases the resistivity of un-doped poly-Si films with rather fine and uniform grain size[6]. This decreases the off-current of the TFTs that use poly-Si as active channel materials. Several authors reported the improvement of the performance in poly-Si after different hydrogenation treatments[7～9], including low energy hydrogen ion implantation[7,8] and plasma treatment[9,10]. However, not all of these methods can passivate defects efficiently, and all of them introduce damage on the surface of poly-Si films. Also, the conventional hydrogenation techniques such as RF glow discharge or ECR plasma treatment are based on trial and error, and they lack controllability and reproducibility. Novel defect passivation methods are of utmost importance in TFT technology.

The poly-$Si_{1-x}Ge_x$ thin films used in this paper were deposited with the reactive thermal chemical vapor deposition (RTCVD) technique[11～15]. The advantages of poly-$Si_{1-x}Ge_x$ prepared by the present technique over conventional CVD poly-Si include low process temperature such as deposition, crystallization, and grain growth. It is also reported that dopant activation occurs at lower temperatures for $Si_{1-x}Ge_x$ than for Si. These enable the application of poly-$Si_{1-x}Ge_x$ in large-area devices such as TFTs. These applications require ohmic contacts in electrodes, which are usually realized with high concentration doping films. In this paper, a novel hydrogenation process by the hot wire technique will be intro-

* Project supported by the Natural Science Foundation of Tianjin (No.043612511), the National Natural Science Foundation of China (No.60437030), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars of the State Education Ministry

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Received 23 August 2006, revised manuscript received 17 October 2006

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duced, and the electrical properties of poly-$Si_{1-x}Ge_x$ films before and after the hydrogenation will be discussed in detail.

2 Experiments

2.1 Hot-wire hydrogenation set-up

An electrically heated filament such as tungsten can effectively decompose gases such as SiH_4 and H_2, and is applied to the deposition of a-Si:H and μc-Si films[16]. Here, in this work, we use the hot-wire method to generate atomic hydrogen for the passivation of defects in poly-$Si_{1-x}Ge_x$ films. Figure 1 shows the experiment setup of the hot-wire hydrogenation used in this work. Hydrogen is introduced into the chamber through a showerhead nozzle and is cracked at a tungsten wire that is resistively heated to temperatures around 1100℃. The filament temperature was measured with a pyrometer. Then, atomic hydrogen generated diffuse into the poly-$Si_{1-x}Ge_x$ films placed under the filament with a distance of 5cm. The sample is set on the grounded substrate platform, which can be heated. As a result, the polycrystalline films are passivated by hydrogen atoms. The typical hydrogenation condition is also shown in Fig. 1. This hydrogenation technique needs no plasma and acceleration voltage, so the damage of the films is minimized during the treatment. Another merit of this technique is that the setup is very simple and easily controlled.

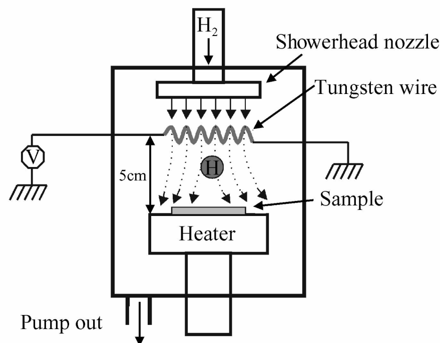

Fig. 1 Schematic diagram of the hot-wire hydrogenation treatment system Typical condition: H_2 flow rate: 400sccm, pressure: 667Pa, T_{fil}: 1100℃

2.2 Electrical characteristic measurement

The conductivities of as-deposited and hydrogenation-treated poly-$Si_{1-x}Ge_x$ films were measured as a function of temperature in coplanar electrode geometry. The lined parallel electrodes of 1cm in length and 0.02cm in gap were formed on poly-$Si_{1-x}Ge_x$ films by vacuum evaporation of aluminum. The conductivity can be derived from as the equation

$$\sigma = \frac{1}{R} \times \frac{l}{Wd} \qquad (1)$$

Here R is the resistance between two electrodes that can be measured, l is the gap length of two electrodes, W is the width of the electrodes, and d is the film thickness.

Generally, as in the case in which one species of carrier dominates the transport, the electrical conductivity σ is simply written as the product of the carrier density n, the charge of an individual carrier q, and the carrier's mobility μ: $\sigma = nq\mu$.

In the simplest version of the high-mobility scheme, the current is carried by a small number of high-mobility carriers, which exist beyond the mobility edge. The equilibrium density of high-mobility carriers is given by

$$n = N(E_c)kT\exp[-(E_c - E_f)/kT] \qquad (2)$$

where $N(E_c)$ is the density of states at the mobility edge E_c. The thermal energy is written as kT, and the Fermi energy as E_f. Also, $E_c - E_f = E_a$, where E_a is the activation energy. The mobility is presumed to be high ($\gg 1cm^2/(V \cdot s)$) and to possess much weaker temperature dependence than that of the carrier density. The conductivity in this model is thus often written as[17,18]

$$\sigma = \sigma_0 \exp[-E_a/kT] \qquad (3)$$

where σ_0 is nearly a constant. For a temperature-independent Fermi level, the conductivity has simply activated temperature dependence. Thus the activation energy can easily be derived from the dependence of conductivity on temperature.

If the hopping conduction through the localized states in amorphous phase or at the grain boundaries dominates the carrier conduction process, the dark conductivity and activation energy will be changed. Consequently, from the measurements of the dark conductivity as a function of temperature, one can obtain some understanding of the carrier transport and the structural properties of the materials. In this work, we investigated the hydrogenation and ion doping effects through studying the change of conductivity and activation energy calculated from the temperature dependence of conductivity before and after the treatment.

2.3 Process of hydrogenation by hot-wire technique

After the sample setting, the chamber was evacuated down to a base pressure of 1.33×10^{-4} Pa by a turbo molecular pump before the hydrogen gas was introduced. During the treatment, the H_2 flow rate was set at 400sccm and exhausted by a rotary pump. The pressure was 667Pa, which is the same as the films deposition condition, and was automatically controlled using a Baratron valve. The filament was electrically heated to a temperature of 1100 ~ 1200℃, which was controlled by a pyrometer. A thermal couple was used to measure the sample temperature. When all the parameters became stable, the shutter between filament and sample was opened and hydrogenation treatment began. As the treatment time passed, the sample surface temperature increased gradually due to radiation of heat from the filament. Figure 2 shows the relationship between the sample surface temperature and hydrogenation treatment

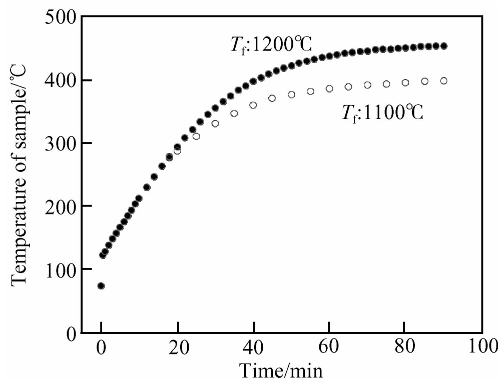

Fig.2 Substrate temperature as a function of hydrogen treatment time at different filament temperatures (Substrate is not heated here.)

time. At a filament temperature of 1100℃, the sample temperature was saturated at about 400℃ after 60min treatment. A filament temperature of 1200℃ caused a higher saturation substrate temperature of about 450℃. It is well known that high temperature annealing will result in desorption of hydrogen from polycrystalline films. Thus the controlling of the substrate temperature is very important in this hydrogenation technique in order to obtain a most suitable hydrogenation effect.

3 Results

3.1 Effect of filament temperature

Figure 3 shows the reciprocal temperature plot of the conductivity of the non-hydrogenated and hydrogenated poly-$Si_{1-x}Ge_x$ films measured in the range between room temperature and 110℃. The hydrogenation treatments were carried out for 70min under two conditions with different filament temperatures of 1100 and 1200℃. To ensure the comparison's reliability, all the samples used in this paper were deposited under the same conditions, as listed in Table 1. The film thickness is 200nm with a grain size of about 50nm. As-deposited film has a dark conductivity of about 10^{-4}S/cm and an activation energy of 0.40 ~ 0.44eV. After 70min hydrogenation at a filament temperature of 1100℃, the conductivity decreased to 1.0×10^{-5}S/cm and activation energy increased to 0.55eV. These values are similar to the bulk c-Si, indicating that hot-wire hydrogenation treatment can effectively passivate the defects. Hydrogenation treatment with a filament temperature of 1200℃ destroyed the film's characteristics as shown in Fig.3. From Fig.2 we can see that hydrogenation for 70min at a filament temperature of 1200℃ resulted in a substrate temperature higher than 450℃. This temperature is too high and causes the desorption of hydrogen from the films. As a result, the electrical properties were destroyed. From the above experimental results, we conclude that a substrate temperature under 400℃ is suitable for preventing the degradation of electrical characteristics during the hydrogenation treatment.

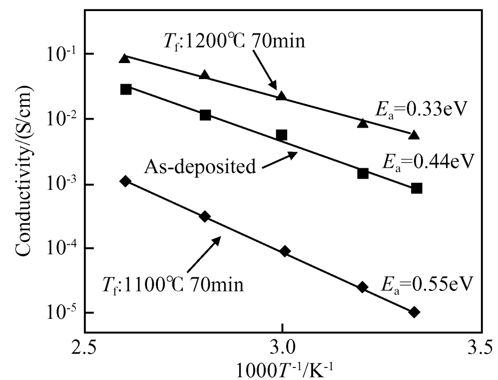

Fig.3 Hydrogenation effect dependence on filament temperature　The H_2 flow rate is 400sccm, and the pressure is 667Pa.

Table 1 Deposition conditions of the poly-$Si_{1-x}Ge_x$ films

Parameter	Value
Substrate temperature	450℃
Pressure	667Pa
Gas flow rate of Si_2H_6	3.0sccm
Gas flow rate of GeF_4	0.3sccm
Gas flow rate of He	1000sccm
Film thickness	200nm
Grain size	～50nm

3.2 Effect of hydrogenation time

Figure 4 shows the conductivity change as a function of hydrogenation time. When the substrate is not heated, the conductivity decreases slowly with the hydrogenation time and reaches a saturation value at about 70min. At this time, the substrate temperature is increased to 400℃. As can be seen, heating the substrate at 350℃ can effectively reduce the hydrogenation time. The 5min hydrogenation treatment resulted in the same hydrogenation effect as 70min treatment without heating. This indicates that the increased substrate temperature can promote the hydrogenation effect due to enhanced diffusion of hydrogen in the film.

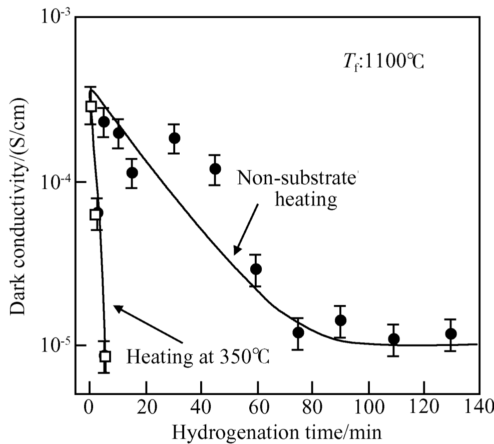

Fig.4 Dependence of dark conductivity on hydrogenation time H_2 flow rate: 400sccm, pressure: 667Pa

However, the controlling of substrate temperature is difficult due to the radiation of heat from the filament, especially when the substrate is heated. As mentioned above, the substrate temperature must be controlled below 400℃ to suppress hydrogen desorption from the film. If no heating is applied to the substrate, the substrate temperature will reach a saturation value of 400℃ after 70min treatment. However, when the substrate is heated at 350℃, the saturation temperature increases quickly and the time to reach 400℃ is shortened. Figure 5 shows the reciprocal temperature plot of the dark conductivity of poly-$Si_{1-x}Ge_x$ films with various hydrogenation treatment times when heating the substrate at 350℃. The results are listed in Table 2. After a 10min hydrogenation treatment, the conductivity increased and activation energy decreased, indicating no more hydrogenation effect. Based on these discussions, we determine that there is a trade-off between the substrate temperature and the treatment time. A low substrate temperature requires a long treatment time to reach a saturated hydrogenation effect and results in easy control, while a high substrate temperature can reduce treatment time, but it is difficult to obtain an optimized result. The best method is to adopt a moderate substrate temperature to control the hydrogenation time between 20～30min.

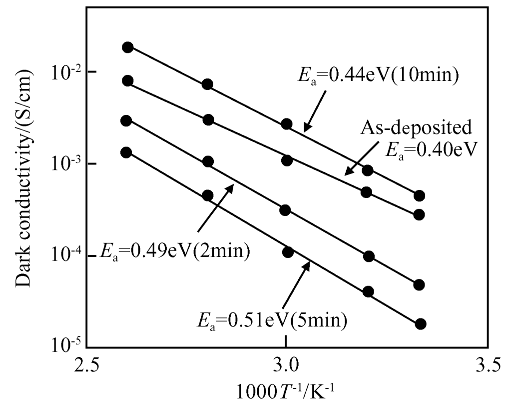

Fig.5 Reciprocal temperature plot of the dark conductivity of poly-$Si_{1-x}Ge_x$ films with various hydrogenation treatment times when the substrate is heated at 350℃

Table 2 Results of hydrogenation at various treatment time when heating at 350℃

Sample		Final T_{sub}/℃	Conductivity /(S/cm)	Activation energy/eV
As-deposited		—	2.8×10^{-4}	4.0
Hydrogenation	2min	370	4.8×10^{-5}	4.9
	5min	390	1.7×10^{-5}	5.1
	10min	450	4.5×10^{-4}	4.4

This time we set the substrate temperature at 150℃ before the hydrogenation starts. After 20 and 30min treatments, the substrate temperature increases to 350 and 400℃, respectively. Figure 6

shows the reciprocal temperature plot of conductivity for these samples. The conductivity and activation energy increased greatly after a 20min treatment. The 30min treatment only increases a little more than the 20min one in conductivity, while almost no more activation energy improvement can be found. This indicates that a 30min hydrogenation treatment is sufficient to passivate defects at this condition.

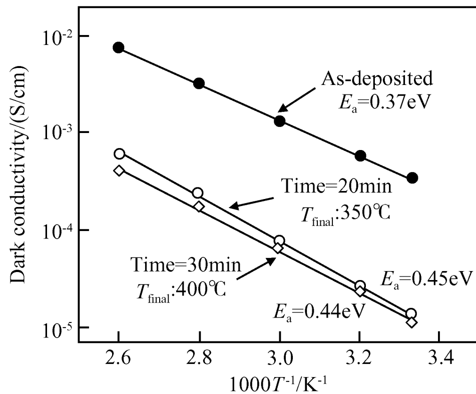

Fig. 6　Reciprocal temperature plot of conductivity for various hydrogenation-treated poly-$Si_{1-x}Ge_x$ films (Hydrogenation condition: H_2: 400sccm, pressure: 667Pa, T_f: 100℃, T_{sub}: 150℃)

4　Discussion

The electrons in the mid-gap states will be excited to the band tail states, and hop to the other nearest band tail states. According to the hopping theory[19], the conductivity by the nearest-neighbor hopping, σ_h, is

$$\sigma_h = \sigma_{h0} \exp(-E_h/kT) \quad (5)$$

where σ_{h0} is the pre-exponential factor depending on the density of the effective defects, and E_h is the activation energy corresponding to an energy difference between the bottom level of a conduction band tail and the Fermi level.

If the effective defect density decreases after the hydrogenation, σ_{h0} and σ_h will decrease because of the decrease of the hopping probability. We should consider both the mid-gap states and band tail states as the defects that contribute to the hopping conduction. In this way, we believe that the hydrogenation-induced decrease of the band tail states and preferential decrease of the acceptor-type mid-gap states will cause an increase in the resistivity of undoped poly-$Si_{1-x}Ge_x$ films near room temperature. Also, the decrease of the mid-gap state causes an increase in activation energy.

5　Summary

In this paper, we established an optimized condition for passivating the defects by the hot-wire technique. The effect of hydrogenation was estimated by investigating the dark conductivity and activation energy derived from the conductivity as a function of temperature. The result shows that this technique can effectively reduce defects in poly-$Si_{1-x}Ge_x$ films. By optimizing the substrate and filament temperatures, the treatment can be accomplished in a short time of 20～30min, which is considerably shorter than other hydrogenation techniques.

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热丝法氢处理多晶硅锗薄膜*

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摘要： 优化了热丝法氢处理多晶硅锗薄膜工艺条件.通过测试材料暗电导的温度特性得出多晶硅锗材料的电导激活能,从而考察氢处理效果.结果表明,采用此技术可有效减少多晶硅锗薄膜中的缺陷态.在优化氢处理时衬底和热丝的温度后,可以把处理时间缩短致 30min 之内,明显短于其他氢处理技术.

关键词： 热丝法；氢处理；多晶硅锗
PACC： 7360J；6780M；8140R
中图分类号： TN304.055 **文献标识码：** A **文章编号：** 0253-4177(2007)03-0317-06

* 天津市自然科学基金(批准号:043612511),国家自然科学基金(批准号:60437030)和教育部留学回国人员科研启动基金资助项目
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2006-08-23 收到,2006-10-17 定稿
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