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H. Ehsani, I. Bhat, J. Borrego, R. Gutmann
(Contact E. Brown)

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CHARACTERISTICS OF DEGENERATELY DOPED SILICON FOR SPECTRAL CONTROL IN THERMOPHOTOVOLTAIC SYSTEMS

H. Ehsani, I. Bhat, J. Borrego and R. Gutmann
Center for Integrated Electronics and Electronics Manufacturing &
Department of Electrical, Computer and Systems Engineering
Rensselaer Polytechnic Institute, Troy, NY 12180-3590

and

E. Brown, R. Dzeindziel, M. Freeman and N. Choudhury
Lockheed-Martin, Schenectady, NY 12301

ABSTRACT

Heavily doped Si was investigated for use as spectral control filter in thermal photovoltaic (TPV) system. These filters should reflect radiation at 4 μm and above and transmit radiation at 2 μm and below. Two approaches have been used for introducing impurities into Si to achieve high doping concentration. One was the diffusion technique, using spin-on dopants. The plasma wavelength (λ_p) of these filters could be adjusted by controlling the diffusion conditions. The minimum plasma wavelength achieved was 4.8 μm . In addition, a significant amount of absorption was observed for the wavelength 2 μm and below. The second approach was doping by ion implantation followed by thermal annealing with a capped layer of doped glass. Implantation with high dosage of B and As followed by high temperature annealing ($>1000^\circ\text{C}$) resulted in a plasma wavelength that could be controlled between 3.5 and 6 μm . The high temperature annealing ($>1000^\circ\text{C}$) that was necessary to activate the dopant atoms and to heal the implantation damage, also caused significant absorption at 2 μm . For phosphorous implanted Si, a moderate temperature (800–900 $^\circ\text{C}$) was sufficient to activate most of the phosphorous and to heal the implantation damage. The position of the plasma turn-on wavelength for an implantation dose of $2 \times 10^{16} \text{ cm}^{-2}$ of P was at 2.9 μm . The absorption at 2 μm was less than 20% and the reflection at 5 μm was about 70%.

1. INTRODUCTION

Photovoltaic (solar) cells are widely used to convert light energy from the sun into usable electrical energy through a direct conversion process. A similar device, the thermal photovoltaic cell or TPV cell, utilizes energy from the near infra-red spectrum to excite charge carriers and create electrical energy. These devices have immense practical value for generating power from sources radiating thermal energy. In this case, only those wavelengths corresponding to energies equal to or greater than the bandgap of the TPV cell material are useful. However, the thermal energy source radiates energy at a continuum of wavelengths corresponding to black body radiation¹. All wavelengths below the bandgap energy would pass through the cell and be wasted. To increase the efficiency, the wavelengths corresponding to the sub band gap energies should be reflected back into the source to reduce the input power to the system. These spectral control techniques can be accomplished utilizing a heavily doped semiconductor filter or "plasma filter".

Some semiconductor oxides such as tin oxide⁽²⁾, indium oxide⁽³⁾ and indium tin oxide⁽⁴⁾ have already been developed for use in efficient incandescent lamps⁽⁵⁾ and energy-efficient windows⁽⁶⁾ for houses. However, the characteristics of these filters are not suitable for spectral control in TPV systems. The plasma wavelength of these filters are usually in the 0.8-1 μm ⁽⁷⁾ range whereas, wavelength in the range of 2-4 μm is necessary for efficient TPV systems, depending on the source temperature. Control of the plasma wavelength in semiconductor oxide filters in the range 2-4 μm has been found to be difficult until recently.

This paper focuses the development of degenerately doped Si as plasma filter for TPV applications. The advantages of Si plasma filters (because of the advanced Si technology) are: reproducibility, high doping uniformity on large area wafers, a precise control on the dopant concentration, and the availability of large area wafers. The plasma wavelength can be adjusted over a wide range by varying the dopant concentration in silicon. In this paper, we will describe two methods to introduce impurities in Si, namely, diffusion technique using spin-on-doped glass and ion implantation technique followed by annealing with a cap layer of doped glass. Successful control of the plasma turn-on wavelength in the range 2.5 to 5.5 μm with negligible absorption at lower wavelength was obtained using the latter technique.

2. SIMULATION OF PLASMA FILTER PERFORMANCE

In order to determine the parameters which are important in the design of plasma filters, we have simulated their performance. The model assumed is shown in Figure 1 and it consists of the plasma filter material of thickness t , supported by a substrate of thickness T . In the case of silicon plasma filter the thickness t is the thickness of the heavily doped region since the substrate of thickness T is the lightly doped silicon. The important material parameters of the plasma filter material are its electron density n , its optical relative dielectric constant ϵ_r , and the electron collision frequency ω_c which is determined by the scattering relaxation time.

The simplest case to consider is the one in which there is no free carrier absorption. In this case, the effective electric permittivity of the plasma filter material, ϵ_{eff} , as functions of wavelength is given by:

$$\epsilon_{eff} = \epsilon_r \epsilon_o [1 - (\frac{\lambda}{\lambda_p})^2]$$

where ϵ_r is the optical dielectric constant of the filter material, ϵ_o is the permittivity of free space and λ_p is the plasma wavelength of the material and it is given by⁽⁸⁾

$$\lambda_p^2 (\mu m) = \frac{4\pi^2 \epsilon_o^2 \epsilon_r m^*}{q^2 N} = 1.12 \times 10^{21} \times \frac{(m^*/m) \epsilon}{N (cm^{-3})}$$

In the case of a thick plasma frequency filter ($t \gg \lambda$), figure 2 shows the reflection of a silicon plasma filter as a function of wavelength for several plasma wavelengths. Notice that the transition from zero reflection to total reflection is very sharp and it occurs very close to the plasma wavelength. The relationship between the plasma wavelength λ_p and the doping concentration for silicon is shown in figure 3.

The sharp transition between full transmission and total reflection is due to the long length of the plasma filter material. In figure 4, we show the reflectance characteristics of silicon filters for three different thickness normalized to the plasma wavelength. Notice that the figure shows that it is necessary to have a plasma filter material between 0.1 to 1 times the plasma wavelength. For thickness below 0.1, the transition from full transmission to total reflection is very gradual. An effect which has not been considered is the one of free carrier absorption. Thick plasma filter material has a higher total absorption, so a compromise has to be achieved between the free carrier absorption and the sharpness of the transition. Free carrier absorption in the transmission

region can be estimated from the absorption coefficient α , given by⁹:

$$\alpha = \frac{N q^3 \lambda^2}{4 \pi^2 \epsilon_o c^3 (m^*/m_o)^2 m_o^2 \mu n} = 5.23 \times 10^{-17} \times \frac{N (cm^{-3}) \lambda^2 (\mu m)}{(m^*/m)^2 n \mu (cm^2/Vs)}$$

where c is the speed of light in free space.

3. EXPERIMENTAL METHODS

The (100) oriented Si wafers used in these experiments were p-type with resistivity in the range of 5-25 ohm-cm, double side polished with the thickness of about 300 μm . Lightly doped silicon was chosen so that residual free carrier absorption in the bulk of the wafer is negligibly small. For doping with diffusion, a spin-on dopant source was first spun on the wafer and the diffusion was carried out in nitrogen atmosphere. For doping with ion-implantation, the wafers were first coated with 200 Å thick thermal oxide and the ion implantation was done through this

oxide. The thin SiO_2 layer should prevent out-diffusion of dopants during annealing. Some wafers were implanted without this SiO_2 layer, in which case they were coated with spin-on doped glass prior to annealing. Both conventional furnace annealing and rapid thermal annealing (RTA) was used. Fourier transform infrared spectroscopy (FTIR) was used to determine the reflection and transmission spectra of the Si plasma filters in the range 1.5-20 μm . The percentage absorption at a particular wavelength was calculated by adding the percentage of reflection and transmission at that wavelength and subtracting from 100. Secondary ion mass spectrometric (SIMS) analysis was conducted to obtain the concentration and the distribution of impurities before and after annealing. Hall measurement was carried out using the Van der Pauw technique to measure the mobility of the carriers.

4. RESULTS AND DISCUSSIONS

Diffusion Technique

The first series of experiments were conducted by doping Si with As by the diffusion technique, using spin-on-dopants as the source. Arsenic was used as the dopant source because its diffusion results in an abrupt profile compared to that of phosphorous⁽¹⁰⁾. The long tail in the diffusion profile in the case of phosphorous can significantly increase the free carrier absorption in the plasma filter. The spin-on-dopant (arsenosilicate glass) was applied to the wafers and the diffusion was carried out in the temperature range from 900°C to 1200°C. For temperatures below 1000°C, we did not see any plasma characteristics below 20 μm , indicating insufficient diffusion of dopants into the Si. At the diffusion temperatures above 1000 °C, the plasma behavior of the wafers was observed within the wavelength range of our measurement, 1.5 to 20 μm . Figure 5 shows the reflection and transmission spectra of a Si wafer diffused with As at 1150°C for 2.5 hours. As can be seen, the position of the plasma wavelength is at 4.8 μm and the maximum reflectivity at 10 μm is about 85%. The carrier concentration calculated from the plasma wavelength is about $1.5 \times 10^{20} \text{ cm}^{-3}$. This value is approximately a factor of 10 lower than the solid solubility of As ($1.2 \times 10^{21} \text{ cm}^{-3}$) in Si⁽¹¹⁾ at 1150 °C, indicating that either the diffusion of dopant is limited by the dopant source or a significant amount of As present is electrically inactive. The absorption in these filters was found to be very high (over 60%) as seen in figure 5. The calculate absorption coefficient at 2 μm is about $4.5 \times 10^3 \text{ cm}^{-1}$. The thickness of the doped layer is about 1 μm , based on the time and temperature of the diffusion. Therefore, the total absorption at 2 μm should be less than 40%. We believe that the extra absorption is caused by the defects generated by As or Si-As precipitates that may be present at the doped region. Various diffusion time and temperatures were investigated, and the minimum value of the plasma wavelength was only 4.8 μm and high absorption was common in all these wafers. Therefore, an alternative to diffusion technique was investigated.

Ion Implantation

Ion implantation is a standard technique being used in silicon microelectronic industry for introducing precise amount of dopants into Si wafers. However, the doping range being used is not high enough so that some modification of the standard technique is necessary in order to get

high doping near the surface. The annealing condition also need to be optimized to get very abrupt doping profile in order to minimize free carrier absorption. In this section, the characteristics of plasma filters fabricated using ion implantation technique will be described. As and P were implanted to get n+ layers on undoped Si, whereas B was implanted to get p+ layers.

Arsenic Implantation

The high resistivity Si wafers were implanted with 150KV As with dosage in the range $1-5 \times 10^{16} \text{ cm}^{-2}$ and then thermally annealed to activate the dopants and to heal the implantation damage. A 200 Å thick thermal oxide was grown on some of the wafers prior to ion-implantation so that out-diffusion of As can be prevented during post-implantation annealing. Both furnace annealing and rapid thermal annealing (RTA) were used. The results are summarized in Table I. As shown in Table I, furnace annealing at 1000°C for 30 minutes resulted in filters with plasma wavelength at 6 μm, independent of the implantation dose. We believe that 1000°C annealing is not high enough for the complete removal of implantation damage, so that the effective carrier concentration is determined by the residual damage rather than the implantation dose. Table I also shows the results obtained from layers annealed at 1200°C for 5 minutes in an RTA system. As can be seen, the plasma wavelengths varied with the implantation dose and reached as low as 4.5 μm for samples implanted with a dose of $5 \times 10^{16} \text{ cm}^{-2}$.

Arsenic has high vapor pressure and significant out diffusion of As can occur during the high temperature annealing, even though a 200 Å thick SiO₂ is present. To prevent the possibility of As out diffusion, some of the implanted wafers were etched in HF to remove the thermally grown SiO₂ that was deposited before ion-implantation and then coated with a 0.25 μm thick spin-on As-doped glass (arsenosilicate glass) prior to annealing. This doped glass can also be a source of As for diffusion during annealing. As shown in Table 1, the plasma wavelengths of these filters occurred at a lower value compared to those annealed without the presence of the doped glass. In addition, RTA resulted in filters with plasma wavelength at a lower value compared to those annealed in a furnace. This difference could be caused by the higher redistribution of As in furnace annealing. The plasma wavelength was even lower for samples annealed for 2 minutes at 1200°C using RTA. Shorter annealing time apparently causes less redistribution of dopants, so that peak carrier concentration is higher in these samples. We have not observed any significant improvement on the plasma characteristics of the wafers annealed between 1 to 2 minutes. Figure 6 shows the reflection and transmission spectra of As-implanted layer annealed at 1200°C for 2 minutes in RTA with a cap layer of doped glass. Note that the reflectivity at 10μm reaches 90%, but the absorption at 2 μm is about 28%. These results indicate that the redistribution and out diffusion of dopant impurities should be minimized to obtain low value for λ_p , with minimum free carrier absorption. All further studies were conducted using RTA system with the doped glass as the cap layer.

The plasma wavelength and the total absorption at 2μm of As doped layer as a function of the implantation dose was carried out and the results are summarized in Figure 7. All the wafers were annealed for 2 minutes at 1200°C. This figure indicates that the plasma wavelength shifts to lower value as the implantation dose increases from $1 \times 10^{16} \text{ cm}^{-2}$ to $5 \times 10^{16} \text{ cm}^{-2}$. With a

further increase of the dose, the plasma wavelength moves to higher wavelengths.

Low absorption by the plasma filters is also important for efficient performance of TPV systems. As seen in Figure 7, the absorption increases as the As concentration increases, with significant absorption observed for implantation doses above $5 \times 10^{16} \text{ cm}^{-3}$. The increase of both the absorption and the plasma wavelength beyond $5 \times 10^{16} \text{ cm}^{-3}$ dose could be caused by the defects generated by the precipitation and local chemical reaction of As and Si. This reaction can decrease the carrier concentration and can generate a high density of defects. Therefore, the absorption is not due to just the free carriers, but also due to defects.

In order to investigate the concentration and distribution of dopant impurities before and after annealing, SIMS measurements have been conducted. SIMS analysis was performed on wafers implanted with $2 \times 10^{16} \text{ cm}^{-2}$ dose of As. Figure 8(a) shows the SIMS data before annealing and figure 8(b) is the SIMS profile after the wafer was annealed at 1200°C for 2 minutes. It is interesting to observe that the total amount of As in the wafer increased after the short annealing and that As diffused deep up to $0.9 \mu\text{m}$. The As concentration was about $6 \times 10^{20} \text{ cm}^{-3}$ with the peak concentration occurring near the surface indicating that the excess As comes from the doped glass. Since implanted region is highly defective or even amorphous, high diffusion rate for As is expected in the ion implanted layer. If we assume 100% activation, the plasma wavelength should be lower and the percentage absorption should be higher than the values obtained by experiments, indicating incomplete As activation.

The Hall mobility of $27 \text{ cm}^2/\text{V}\cdot\text{sec}$ was obtained on a Si wafer implanted with As with the dose of $2 \times 10^{16} \text{ cm}^{-2}$, annealed at 1200°C for 2 minutes.

Phosphorous Implantation

Since As implanted layers required high temperature annealing for significant activation and had relatively high absorption at $2 \mu\text{m}$, P was investigated for doping. Phosphorous implantation was carried out at 120 kV , with the dose in the range $1-10 \times 10^{16} \text{ cm}^{-2}$, followed by annealing in RTA system. Prior to annealing, the implanted wafers were etched in dilute HF solution to remove any oxide and a $0.24 \mu\text{m}$ thick layer of P-containing doped glass was applied by the spin-on technique.

Figure 9 show the plasma wavelength and the total absorption at $2 \mu\text{m}$ as the annealing temperature was varied over a wide range. These annealings were carried out using RTA for 2-5 minutes in nitrogen ambient. Both the plasma wavelength and the total absorption monotonically increases as the annealing temperature is increased. Unlike Si implanted with As, a moderate temperature of about $800-900^\circ\text{C}$ is sufficient to activate implanted P. Phosphorous implanted Si may have less damage to start with because P is lighter than As and the diffusion rate of P is higher than that of As. Therefore annealing at lower temperature may be sufficient to activate P. As the annealing temperature is increased, the plasma wavelength shifted to higher wavelength, caused by the redistribution of P. The absorption also increases with the annealing temperature because it increases exponentially with the thickness. Figure 10 shows a typical reflection and transmission spectra of a Si wafer implanted with P with the dose of $2 \times 10^{16} \text{ cm}^{-2}$, annealed at 850°C for 5 minutes. Absorption at $2 \mu\text{m}$ is less than 25% (without anti-reflection coating) and

the total reflection at 10 μm is more than 85%.

Figure 11 show the effect of implantation dose on the plasma wavelength and the total absorption at 2 μm , for wafers annealed at 850°C for 5 minutes in an RTA system. As the implantation dose is increased from 1 to 3 $\times 10^{16} \text{ cm}^{-2}$, the plasma wavelength decreases and the total absorption increases, as expected. Beyond 3 $\times 10^{16} \text{ cm}^{-2}$, the data indicate that the low annealing temperature is not sufficient to fully activate the implanted phosphorous. The variation of both the plasma wavelength and the absorption in the range of implantation dose studied is not large, so that either of these wafers will be a good filter for TPV systems.

Figures 12(a) and 12(b) show the SIMS profile of P in Si before and after rapid thermal annealing, respectively. Unlike Si implanted with As, the gaussian distribution of the P dopant remain gaussian after the annealing, with a small increase of the width of the profile. This indicates that annealing at 850°C for a short period does not redistribute phosphorous atoms significantly, but is high enough to activate phosphorous. On the other hand, high temperature annealing is required to activate implanted As, which also redistribute As by diffusion.

The effect of implantation energy in the range 90-150 KV on the filter characteristics was also investigated. But, we have not seen a significant difference on the reflection and transmission spectra of these wafers after they have annealed at 850°C for 5 minutes. This results are expected because the changes in energy simply places P at different depths from the surface, keeping the profile essentially the same. In order to obtain a more uniform P distribution, double implantation at two energies (100 KV and 120 KV) was performed. An improvement was seen on the reflection spectra. Since activation-anneal of P does not cause redistribution, improvements in the filter characteristics can be achieved using multiple implantation. These studies are underway and will be reported later.

Hall measurement showed a mobility of 32 $\text{cm}^2/\text{V}\cdot\text{sec}$ for a P-doped sample annealed at 850 °C for 5 minutes. This value is slightly larger than the electron mobility obtained on the wafers implanted with As.

Boron Implantation

Because holes have larger effective mass than that of electrons, p type Si will have less free carrier absorption. Therefore, boron was also investigated as the dopant source. Boron implantation was carried out on bare silicon, and the wafers were annealed in RTA system to activate boron. Prior to annealing, the wafers were coated with spin-on dopant glass to a thickness of 0.24 μm to prevent any possible out-diffusion.

Figure 13 shows the plasma wavelength and the total absorption at 2 μm , as a function of the annealing temperature for wafers implanted with $2 \times 10^{16} \text{ cm}^{-2}$ of boron. Similar to As, high temperature annealing was found to be necessary to activate boron. Since B is a light element, the mechanism for ion stopping during ion implantation is due mostly to electronic stopping. Therefore, the implanted area may not become amorphous, but may remain polycrystalline. Generally, high temperature annealing is necessary to recrystallize polycrystalline materials.

Figure 14 show the effect of the implantation dose on the filter characteristics. These and other results show that activation of B is limited by the solid solubility at high temperatures. If the implantation dose is very high, boron will precipitate during high temperature annealing. These precipitated centers could be the source of defects and high absorption. Figures 15(a) and 15(b) show the SIMS profile of boron in Si before and after 1200°C - 2 minute anneal. As can be seen, significant redistribution of boron is observed after the annealing. The redistribution of B should be negligible if the implanted region were single crystal.

The Hall measurement showed that the mobility of holes in p-type Si is about 28 cm²/V-sec, for the samples implanted with a dose of 2x10¹⁶ cm⁻² and annealed at 1150°C for 2 minutes. Note that similar values were obtained for both p type and n type layers, when the doping concentration is very high.

5. CONCLUSIONS

The plasma behavior of Si heavily doped with As, P, and B was investigated. We have seen that high doping concentration can be achieved by the implantation technique, followed by rapid thermal annealing with a cap layer of spin-on doped glass. High temperature annealing (>1100°C) is necessary to activate significant percentage of As and B. This results in significant redistribution of the implanted species, causing high absorption at 2 μm and below. The high absorption is probably caused by both the free carriers and the defects generated by As and B precipitates. On the other hand, a moderate annealing temperature (800-900°C) was sufficient to activate P in Si. This causes negligible redistribution and hence results in low absorption because the thickness of the doped layer is low. In addition, low temperature annealing doesn't cause P precipitates so that absorption caused by defects is also low. Therefore, P doped silicon shows high promise as a candidate for plasma filter in TPV application. The plasma wavelength for an implantation dose of 2x10¹⁶ cm⁻² of P was at 2.9 μm. The absorption at 2 μm was less than 20% and the reflection at 5 μm was about 70%. Further improvement in filter characteristics can be achieved by optimizing the doping profile using multiple implantation technique at different energies.

6. ACKNOWLEDGEMENT

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TABLE1: Annealing conditions and the properties of the doped layers

Exp. set #	Dose cm^{-2}	Annealing System	Cap	Annealing Temp. ($^{\circ}\text{C}$)	Annealing Time (Min)	$n (\text{cm}^{-3})$	$\lambda_{\min} (\mu\text{m})$ (Turn point)
1	1E16	Furnace	SiO_2 (200Å)	1000	30	9.6E19	6
1	2E16	Furnace	SiO_2 (200Å)	1000	30	9.9E19	5.8
1	5E16	Furnace	SiO_2 (200Å)	1000	30	9.9E19	5.8
2	1E16	RTA	SiO_2 (200Å)	1200	5	7.7E19	6.7
2	2E16	RTA	SiO_2 (200Å)	1200	5	1.2E20	5.4
2	5E16	RTA	SiO_2 (200Å)	1200	5	1.7E20	4.5
3	1E16	Furnace	Arsenosilicate	1150	15	1.3E20	5
3	2E16	Furnace	Arsenosilicate	1150	15	1.6E20	4.7
3	5E16	Furnace	Arsenosilicate	1150	15	1.7E20	4.5
4	1E16	RTA	Arsenosilicate	1200	5	2.1E20	4.9
4	2E16	RTA	Arsenosilicate	1200	5	3.5E20	3.9
4	5E16	RTA	Arsenosilicate	1200	5	6.3E20	3.4
5	1E16	RTA	Arsenosilicate	1200	2	3.7E20	3.8
5	2E16	RTA	Arsenosilicate	1200	2	4.7E20	3.6
5	5E16	RTA	Arsenosilicate	1200	2	7.3E20	3.2

SCHEMATIC DIAGRAM OF PLASMA FILTER

REFLECTANCE OF SILICON

SILICON PLASMA WAVELENGTH

REFLECTANCE OF SILICON PLASMA FILTERS

NORMALIZED WAVELENGTH λ / λ_p

2

1

Fig 7(a)

Fig. 4. 7b

8(0)

8.6

~~Fig~~ 9(a)

Fig 9(b)

Fig 10

Fig 11(a)

Fig. 11(b)

14(a) Fig 12(a)

Fig 12 (b)

Fig #2

Fig 13 (a)

Fig 14 (a)

1510 Fig 15 a)

Fig. 15(b)