Comparison of Hydrogen and Deuterium incorporation in Polysilicon based-Photodetector

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Abstract

The electrical conduction of polysilicon can be improved through passivation of defects located at grain boundaries. Most passivation proceeds by hydrogen boning to dangling bonds of silicon. However, more research is needed on the reliability of the Si-H bond. A process using deuterium instead of hydrogen can be expected to improve the performance of silicon devices. In this study, we have investigated how the deuterium effect appears in polysilicon application. For this purpose, a photodetector composed of a polysilicon film incorporated with hydrogen or deuterium was prepared and then, current-voltage (IV) characteristics, photo response, and degradation thereof were investigated. Hydrogen and deuterium incorporation was performed by both furnace annealing and ion implantation methods. It was found that in order for the passivation effect to occur in polysilicon, the density of grain boundary must be maintained properly, and there must be no additional damage during the hydrogen or the deuterium process. Through this study, it was confirmed that the electrical characteristics and the reliability of the polysilicon based-photodetector were improved by forming a Si-D bond inside the polysilicon by the furnace annealing.

I. Introduction

Polysilicon is widely used in solar cells, displays, micro-electro mechanical systems (MEMS) and sensor applications [1-4]. In most fields, it is used as a material that can replace single crystallite silicon. However, polysilicon is composed of numerous small crystallites (grains) and grain boundaries, and thus exhibits different characteristics from single crystallite silicon. In the conductive properties of polysilicon, the grain boundary acts as a recombination center, so the electrical properties and the reliability of the performance of the polysilicon device depend on the chemical properties of the grain boundary.

In this paper, we investigated the device performance and the reliability in a polysilicon based-photodetector that has experienced hydrogen or deuterium processes. Hydrogen or deuterium bonds are used for the passivation of defects (or dangling bonds) in the grain boundaries of polysilicon. A post-metallization anneal (PMA) using

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deuterium has been introduced to improve the reliability of MOSFETs [5-8]. When the cause of the defect generation in the gate oxide is related to the hydrogen bond in the silicon oxide, it was possible to suppress the defect generation in the gate oxide by replacing the Si-H bond with the Si-D bond. This phenomenon is called as the isotope effect, and this effect can be observed in the hot-carrier degradation of the MOSFET [5]. A comparison of hydrogen and deuterium processes has been widely published for single crystallite silicon devices, but has not yet been published for devices composed of polysilicon.

The total amount of defects within a grain boundary is proportional to the total length of the grain boundary and is inversely proportional to the average size of the grain. In this study, the photodetectors with three types of grain sizes of the polysilicon film were manufactured and their photo response depending on the passivation processes was observed, respectively. Hydrogen or deuterium bonds for the passivation were formed through the furnace annealing and the ion implantation. Finally, we tried to find the isotope effect that can improve the operating characteristics and the reliability of the polysilicon based-photodetector.

Ⅱ. Device Fabrication

About 500-nm-thick undoped polysilicon was prepared by LPCVD. The grain sizes of polysilicon used in the study were 21.4 nm (A sample), 26.0 nm (B sample) and 31.6 nm (C sample), respectively. Through Secondary Ion Mass Spectrometry (SIMS) analysis, it was investigated that hydrogen at a concentration of about $10^{18}/cm^3$ was present inside the as-deposited polysilicon film. Fig. 1 shows the structure of the fabricated polysilicon-based photodetector. About 150-nm-thick silicon oxide film was formed on the surface of the polysilicon. This silicon oxide film is used as an anti-reflection film for light absorption, and can also serve as a buffer filmfor surface damage that may occur during ion implantation. A laminate structure of aluminum (Al) and titanium (Ti) was used as a metal electrode. The finally fabricated photodetector structure has a metal-semiconductor-metal (MSM) structure.

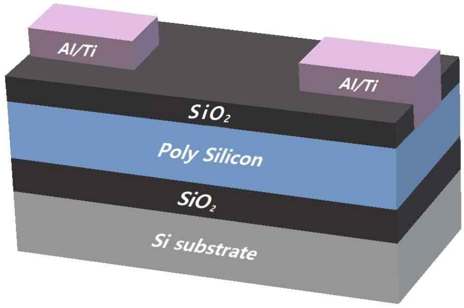

Fig. 1. Schematic diagram of polysilicon based-photodetector.

Annealing process was carried out in hydrogen or deuterium ambient at 1 atm and 400 °C for 30 min. Ion implantation of each ion was processed at the same dose of about $10^{14}/cm^2$ and each incident energy having the same ion range of about 330 nm. After ion implantation, 400 °C annealing was subsequently performed in a nitrogen atmosphere. Hydrogen and deuterium are known to form activation bonds in silicon material at 400 °C [9, 10], so it is considered that the two types of ions could passivate the grain boundary of polysilicon.

The concentrations of hydrogen and deuterium on the surface of polysilicon were maintained similarly, but on the inside of polysilicon, the concentration of hydrogen was rather larger. This is because hydrogen, a by-product generated during the LPCVD process, remains inside the polysilicon. Since the two electrodes are positioned horizontally in the device structure, light energy absorption and photocurrent generation will mostly occur in the upper layer of polysilicon. Therefore, the passivation of grain boundaries near the surface of polysilicon will mainly affect the electrical properties of our device. The photo response of the device were investigated with the ratio of photocurrent and dark current (= I_{photo}/I_{dark}), which was mentioned as the sensitivity (S) in the result data. The illumination was achieved by using a 170 mW light at an 850-nm wavelength from a light-emitting diode (LED).

Ⅲ. Result and Discussion

Fig. 2 shows the sensitivity characteristics of the manufactured MSM device. Here, the sensitivity is the ratio of each dark current and photocurrent measured at 6 V. The sensitivity depended on the grain size of polysilicon, and B sample showed the largest value among the devices. We have previously reported that polysilicon requires an appropriate grain size to be used as a photodetector [11].

From the results of the annealing process, it can be seen that the sensitivity of the photodetector was increasedin the A and B samples by deuterium treatment, but the deuterium effect did not appear in the C sample with relatively large grains. In general, the lower the density of the grain boundary, the smaller the area to be passivated. Hydrogen or deuterium first bonds with silicon dangling bonds at the grain boundary, so the passivation effect may appear differently depending on the density of the grain boundary.

Through the deuterium annealing, both the dark current and photocurrent of the MSM device tended to increase. In particular, the increase in photocurrent was more evident in A and B samples. As a result, the sensitivity of the deuterium annealed-device was increased compared to that of the hydrogen annealed-device. This indicates that the deuterium passivation of silicon dangling bonds is more stable due to the heavy mass of deuterium [5]. And the isotopic interfacial hardening effect of deuterium has also been explained in terms of the vibration mode frequencies of the Si-H and Si-D configurations [12, 13]. In the C sample with large grain, both dark current and photocurrent flowed about 100 times more than other devices. This means that the conduction component of each grain was more prominent than the current suppression of the grain boundary barriers in the IV characteristics.

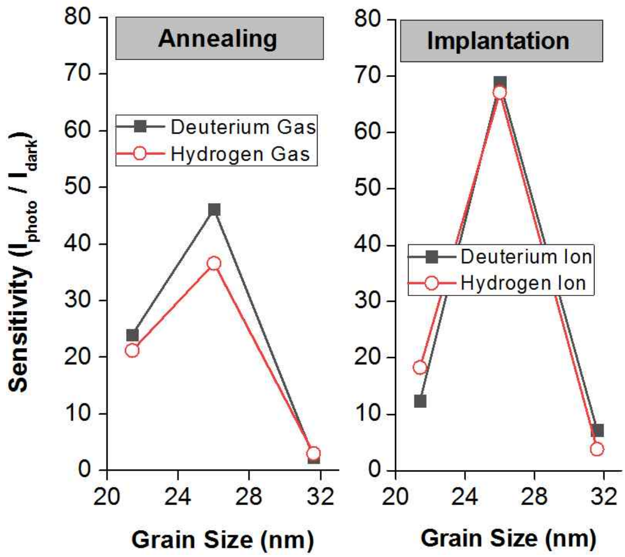

Fig. 2. The sensitivity characteristics of the manufactured MSM device. The sensitivity was measured at the voltage of 6 V.

In the case of ion implantation, it is thought that the IV characteristics of our polysilicon device are more dominantly affected by the amount of defects generated during the process than by the two ion types. Both the dark current and the photocurrent of the deuterium implanted-device tended to be slightly decreased compared to that of the hydrogen implanted-device. This is because more polysilicon surface damage occurred when deuterium ion was implanted. Through SRIM Monte Carlo simulation [14], it was found that displacements per atom (dpa) increased about 2 times in deuterium ion implantation compared to hydrogen ion implantation. Due to these results, it was difficult to directly compare the isotope effect by the two different ions.

When a voltage is applied between two terminals of undoped polysilicon, an electric field appears at each grain and grain boundary. If hydrogen or deuterium passivation bonds are disrupted by strong electric fields or long-term stress, new defects and/or dangling bonds can be created at grain boundaries. Referring to the crystallite/amorphous/crystallite structure model, which is a grain boundary model of polysilicon [15], and the interface model of the metal-oxide-semiconductor (MOS) structure [16], we proposed a hydrogen related-defect generation model in polysilicon as follows. Hydrogen is bonded to trivalent silicon, but the model by deuterium can be explained by substituting Si-D for Si-H.

$\equiv$Si-H + e^- $\rightarrow$Si°+ H_2 : at the grain boundary (1)
Si$\equiv$Si-H + h^+ $\rightarrow$Si$\equiv$$Si^+$: in the grain (2)
Si$\equiv$Si-H + e^- $\rightarrow$Si$\equiv$Si° : in the grain (3)

Here, electron (e^-) and hole (h^+) are carriers of dark current or photocurrent. In the equation, Si° exists as a dangling at the grain boundary and as a neutral electron trap in the grain. These lead to trapping of the hole. Si^+ becomes a fixed charge with a (+) charge.

The variation of sensitivity before and after constant voltage stress may indicate the reliability characteristics of the device. Reproduction of defects due to breakage of the passivation bonds can lead to changes in current conduction. Minor fluctuations occurred in both the dark current and the photocurrent curves measured after the stress, and this appears as a variation in the sensitivity property. The fluctuation in the IV curve means that carrier trapping and/or de-trapping occurs irregularly at the grain boundary [17, 18]. This phenomenon appeared more dominantly in the dark current curve, so the sensitivity value after the stress was distributed in a wide range.

Comparing the devices annealed in hydrogen and in deuterium ambient, it can be seen that the distribution range of the variation of sensitivity is relatively reduced in both A and B samples that have been incorporated with the deuterium, so the reliability of these devices was improved. However, the effect of deuterium annealing did not appear in the C sample with large grains.

In the ion implanted-devices, there was no clear reduction of the range in the variation of sensitivity distribution according to the use of deuterium ion. As the amount of defects on the polysilicon surface increased by using the deuterium ion implantation, we could not find the effect on improving device reliability by using deuterium instead of hydrogen.

The dark current at the passivated polysilicon grows unstable over the stress time. The instability is due to the release of passivation bonds and then, the reproduction of trap charges over time at the grain boundaries. However, grain boundary traps inactivated by the strong passivation will not contribute to the decrease of dark current flow for voltage stress duration. Fig. 3 shows the dark current instability of the hydrogen and the deuterium annealed-photodetectors for the B sample. The inset represents the variation of dark current (ΔI/I) for the corresponding devices. The increase in dark current during the stress means that passivation is strongly maintained at the gran boundary. In Fig. 3, the deuterium annealed-device shows a larger ΔI/I than that of the hydrogen annealed-device, confirming that the grain boundary passivation is strongly maintained.

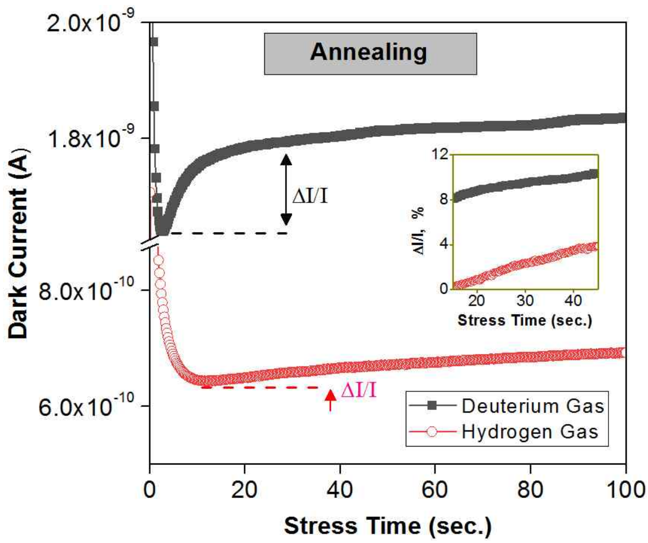

Fig. 3. The dark current instability of the hydrogen and the deuterium annealed-photodetectors. The inset shows the variation of dark current (ΔI/I) for the corresponding devices.

Ⅳ. Conclusion

In this study, a photodetector composed of polysilicon was manufactured, and then hydrogen or deuterium was incorporated into the polysilicon to investigate the isotope effect. The grain boundary passivation, such as Si-H or Si-D bond, was carried out through the furnace annealing and the ion implantation, respectively. Relatively excellent operating and reliability characteristics were found in the device annealed in deuterium ambient. From these results, we could confirm the isotope effect in polysilicon based-device. However, since Si-D bonding in polysilicon mainly occurs at the grain boundary, the isotope effect appears only when the density of the grain boundary is properly maintained. In the device processed with ion implantation, it was difficult to find the isotope effect as the cause of surface damage and current decrease due to the collision of the heavy mass of deuterium ions. Therefore, through the annealing process, the deuterium diffused into the polysilicon, resulting in an isotopic interfacial hardening effect at the grain boundary, and finally, the reliability of the polysilicon based-photodetector could be improved.

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