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Amorphization of Silicon by 250 keV Electron Irradiation and Hydrogen Annealing

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Abstract - We observed that optical properties of silicon changed under high dose electron irradiation at 250 keV. Our experimental results revealed that the optical transmission through a silicon wafer is significantly increased by electron irradiation. Transmission increase by the change in the absorption coefficient is explained through an analogy with amorphous silicon. Moreover, solar cell open-circuit voltages indicated that defects were generated by electron irradiation, and that the defects responded to annealing. Our results demonstrated that the optical properties of silicon can be controlled by a combination of electron irradiation and hydrogen annealing.

Keywords: electron irradiation, hydrogen annealing, optical transmission, silicon defects

1. Introduction

There have been intensive research efforts to combine optics and electronics in semiconductor devices, and the optical properties of silicon became a highly focused subject due to the possibility of this application [1-3]. Crystalline silicon and amorphous silicon demonstrate radically different optical characteristics. Amorphous silicon has greater band-gap energy, which is proportional to hydrogen concentration. The optical absorption of amorphous silicon resembles that of a direct gap material. Amorphous silicon is usually fabricated by plasma enhanced chemical vapor deposition (PECVD), or by ion implantation at high doses. In this paper we studied how the optical properties of crystalline silicon changed under high dose, 250 keV electron irradiation. We observed that optical transmission through the irradiated silicon wafer was increased, and we explicate this as a result of silicon lattice relaxation.

High-energy (above 2 MeV) electron or proton irradiation has been used in silicon power devices to reduce turn-off time and energy loss during switching [4]. When a silicon power device is turned off, excess minority carriers are removed slowly, because silicon is an indirect gap material with carrier recombination times of order of milliseconds. Although irradiation energies above 2 MeV are generally used, we demonstrated that 250 keV electron irradiation can be a candidate for silicon power device irradiation [5-7]. In addition to low cost, 250 keV irradiation has other advantages, compared to either heavy metal diffusion or high-energy irradiation. Pt diffusion has been used in various industries, but analysis has shown that only a small fraction of the Pt diffuses to its required position in the bulk. 2 MeV electron irradiation creates a nearly uniform defect profile across the wafer, and this increases resistance at locations where lifetime control is not needed. In contrast, 250 keV electron irradiation generates defects within 150-μm depth from the front side. Hence, resistance in the vertical direction is lower than that from 2 MeV electron irradiation, and this lower resistance is an important advantage for power devices.

Hydrogenated amorphous silicon (a-Si:H) can be considered an extreme case of silicon with very high defect density [8, 9]. The carrier recombination time in a-Si:H is in the order of nanoseconds, due to the high defect density. Carrier recombination characteristics in irradiated silicon and amorphous silicon are similar, since the slow recombination is accelerated by defects.

In analogy with the recombination characteristics, we can imagine that the optical properties of silicon may be altered by electron or proton irradiation. Defects made by proton irradiation have a narrow implantation profile of a few microns in width, so that the change in optical properties may not easily be observed. In this study, we illustrate that optical transmission and solar cell voltages of silicon can be changed subsequent to a high dose of electron irradiation.

2. Experiments

2.1 Optical transmission in electron irradiated silicon wafers

For optical transmission measurements we used both p-

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type and n-type silicon wafers, grown by the Czochralski method. The p-type wafers were boron doped with 10 Ωcm resistivity, and wafer thickness of 550 μm, and the n-type wafers were phosphorus doped with 2 Ωcm resistivity, and thickness of 730 μm. The electron irradiation energy was 250 keV, at electron doses of either $10^{17}/cm^2$ or $10^{18}/cm^2$, and irradiation was performed in the atmosphere under N_2 flow. After irradiation, the wafers were annealed in N_2 or H_2 atmospheres for one hour, at temperatures ranging from 300-450°C. Optical transmission and reflection were measured between 500 nm and 1500 nm wavelengths. The optical transmission varied when different irradiation and annealing conditions were employed. However, the reflection from the surface remained almost constant, regardless of irradiation and annealing conditions. The reflection at the 1100 nm wavelength was 34%, and remained at this value within 1% for different wafers.

Fig. 1 compares transmissions in p-type silicon wafers, annealed in H_2. Irradiation increased the optical transmission below 1.1 eV by a factor of 5, as evidenced by the increase from 2% to 10% in the long wavelength region above the 1100 nm wavelength (the silicon bandgap energy 1.1 eV corresponds to the 1130 nm wavelength). Unirradiated silicon indicated about 2% light transmission in the same region. Annealing at 450°C resulted in higher transmission than at 350°C. Irradiated wafers without annealing also showed a transmission increase, albeit lower than that of H_2 annealed wafers.

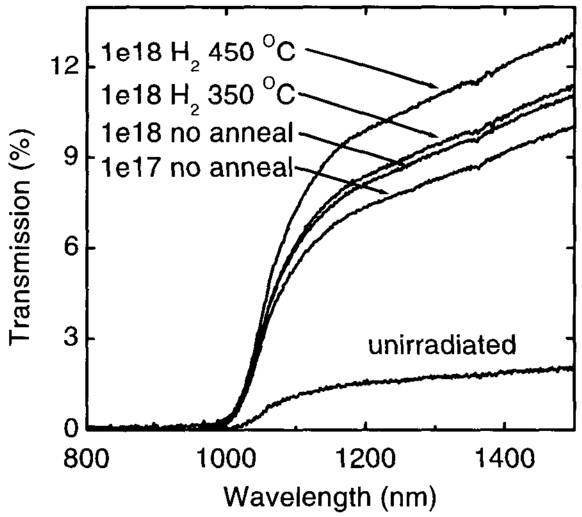

Fig. 1 Optical transmission in p-type silicon wafers. Electron irradiated wafers demonstrate greater transmission.

Transmission increase in the extended wavelength region (Fig. 1) is likely due to changes in the optical properties in the upper part of the wafer, mostly affected by electron irradiation and H_2 annealing. The electron irradiation defect profile was calculated using the EDMULT program [10]. Calculations for 250 keV electrons indicate that the peak of defect density is located about 80 μm from the surface, and that half of the maximum density is located at a depth of approximately 150 μm. The interpretation of the transmission experiments takes this profile into account. Indeed, if the irradiated upper part features a higher transmission, the thickness of the light absorbing layer is effectively decreased and the overall transmission increases. We independently confirmed that the optical properties of the lower portion of the wafer remained unaltered by irradiation, by measuring the switching speed of silicon diodes irradiated on the wafer's backside. In the short wavelength region, the transmission does not display any increase (Fig. 1), because the much greater thickness of the unmodified lower part of the wafer prevents any transmission of the short wavelength light.

Fig. 2 reveals that the transmission change is affected by the annealing gas and by the electron dose. For both 10^{18} /cm^2 and 10^{17} /cm^2 electron doses, H_2 annealing results in a higher transmission than N_2 annealing. The figure also demonstrates that the higher dose (10^{18} /cm^2) results in a higher transmission. At a higher dose, more defects are generated by the irradiation, and, in the case of H_2 annealing, more H_2 can combine with the silicon during the annealing step. It is clear from this figure that the annealing gas is an important factor in determining transmission.

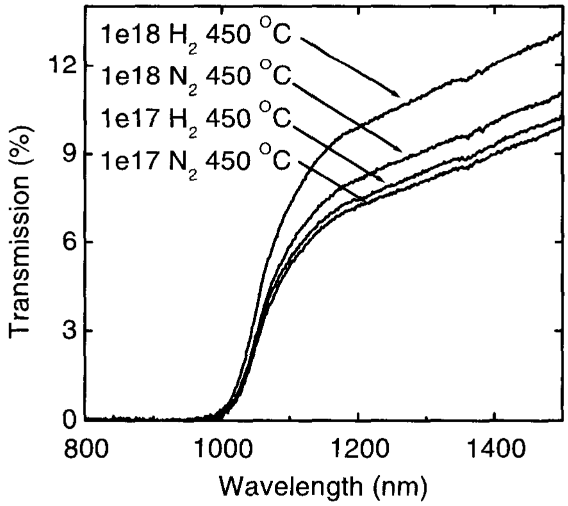

Fig. 2 Transmission change as a function of dose and annealing gas.

Fig. 3 presents the transmission of wafers annealed in hydrogen plasma at 300°C for 1 hour. The electron dose was 10^{18} /cm^2, and the microwave power, 1.2 W/cm^2. It is well known that hydrogen plasma reacts more vigorously with defects than H_2 alone. Yet, in our case the wafer annealed at 450°C H_2 without plasma shows the higher transmission. In the figure, an unirradiated wafer does not demonstrate any change when annealed, neither in H_2 alone nor in the hydrogen plasma. From this figure, we can see that electron irradiation and subsequent annealing in H_2 gas is the most effective way to increase light transmission.

Fig. 1 to 3 contain results measured on boron doped p-type silicon wafers. Fig. 4 presents the transmission measured in phosphorus doped n-type silicon wafers. The thickness of the n-type wafer is 730 μm, so that the relative change in transmission is smaller than that for the thinner p-type wafers. Importantly, in n-type wafers the use of either H_2 annealing or N_2 annealing does not result in many different optical transmissions. The N_2 anneal now causes slightly higher transmission than the H_2 anneal. We propose that this difference can be related to the location where the hydrogen attaches in the silicon. Ref. 4 shows that the hydrogen atom combines with the boron atom in p-type silicon, and with the silicon atom in n-type silicon.

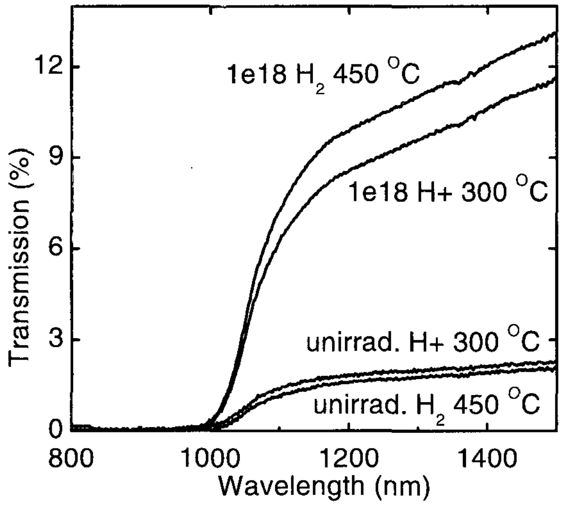

Fig. 3 Comparison of H_2 annealing and hydrogen plasma annealing. Without electron irradiation, transmission in the extended wavelength region is approximately 2%.

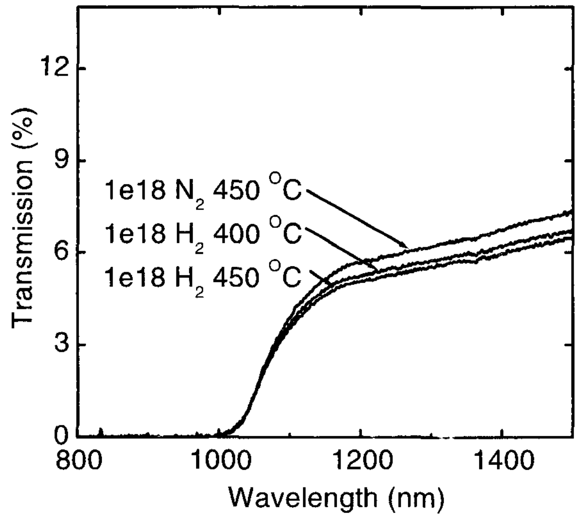

Fig. 4 Optical transmission in n-type silicon wafers. The wafer thickness is 730 μm, so that the relative change is smaller than that in previous figures.

2.2 Solar cell open circuit voltage

We measured the open circuit voltages of irradiated silicon solar cells, to evaluate the effect of electron irradiation and annealing. Fig. 5 indicates the open circuit voltages (V_{OC}) of irradiated silicon solar cells, measured under tungsten lamp illumination at a fixed power level. The solar cells consist of an n^+p structure, fabricated on p-type polycrystalline silicon utilizing a ribbon type casting method. Electron irradiation was performed after metal contacts were fabricated. Irradiation energies between 10 and 250 keV were used, and the doses were 10^{18} /cm^2 at 250 keV, and $5x10^{18}$ /cm^2 at all other energies. The two points at 0 keV correspond to data obtained on unirradiated solar cells. In irradiated but unannealed solar cells, V_{OC} is greatly decreased (lowest curve). The decrease is due to the shorter diffusion length resulting from the high defect density. When annealed in H_2 or N_2, V_{OC} increases, because a portion of the irradiation defects is passivated.

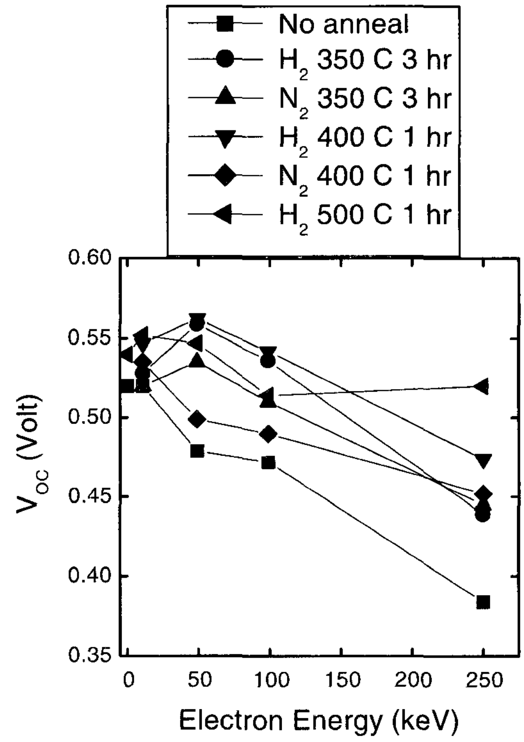

Fig. 5 Open circuit voltages measured in silicon solar cells, irradiated at different electron energies.

For the lower energies (50 keV), H_2 annealing always produces higher voltages than does N_2 annealing. The defects generated at 50 keV are rather shallow, and can therefore readily react with the annealing gas. Upon increasing the electron energy, the generated defects appear in deeper regions, and the annealing gas needs to diffuse deeper for the reaction to occur. In ref. 11, it was estimated that hydrogen could diffuse ~30 μm by annealing at 500°C for 1 h. This explains why the solar cells irradiated at a higher energy (250 keV) illustrate a less systematic dependence on the annealing gas.

These results are consistent with the interpretation of transmission experiments discussed above, where higher temperature H_2 annealing leads to more transmission. The x-ray diffraction pattern measured in ion-implanted silicon showed high density of dangling bonds [12]. We think that these broken bonds by irradiations react with hydrogen during annealing [7]. In a-Si:H, the bandgap energy increases with hydrogen concentration, and a-Si:H solar cells show higher voltages than crystalline silicon solar cells. As a correlation, we explain that the reason for the voltage variations in Fig. 5 lies in the differing hydrogen contents of the samples.

3. Conclusion

Our experiments on the optical transmission through silicon wafers reveal that electron irradiation and subsequent hydrogen annealing modifies the optical properties of silicon. Supporting measurements of solar cell open circuit voltages demonstrate that the crystal structure is deformed by 250 keV electron irradiation. The optical property change we observed could be the result of strain, which was introduced by irradiation and annealing. When hydrogen was inserted into the Si-Si bond broken by irradiation during the annealing, the Si lattice expanded [13]. This expansion will cause tensile strain in the top layer, and optical properties may change as a result. The role of hydrogen is unclear at this point. It is evident that hydrogen is not working as a passivating agent, since hydrogen escapes at 450°C annealing. Our data suggest that hydrogen assists lattice relaxation of damaged crystal structure, and that silicon is transformed into a new structure as a result of this relaxation. However, additional work is required to clarify this point. The solar cell results reveal that defects are generated at energies as low as 50 keV. By utilizing electron irradiation, an amorphous layer can be fabricated at a specified location on a silicon chip. This method can be applied to useful functions when a larger optical signal transmission on the chip is required at high frequencies.

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