PHOSPHORUS DEACTIVATION PROCESS IN SILICON SUBMITTED TO HYDROGEN PLASMA

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ABSTRACT

C-V measurement is an efficient method to determine the active doping concentration in silicon. In this study, we use it in the aim to understand the process which govern the phosphorus deactivation by hydrogen. To do this, the hydrogenation experiments were carried out in hydrogen plasma generated in an electron cyclotron resonance system (MW-ECR) using microwave power (P_{MW}) for a fixed parameters like hydrogen flux, process time and hydrogenation temperature. The hydrogenation revealed a dopant deactivation due to the formation of phosphorus-hydrogen bonding (PH) as evident from the changes in the doping level after hydrogenation of schottky diode made using FZ-single crystalline silicon. It was also found that deactivation of phosphorus was more pronounced at low microwave plasma power and for samples with low initial phosphorus concentration. On the other hand, the formation of molecular hydrogen below the silicon surface called platelets increase with increasing the initial phosphorus concentration. Therefore, the increase of the average platelets size decreases the density of atomic hydrogen and in turn lowers the effective hydrogen diffusivity.

Key Words: *Phosphorus Deactivation Profile, Plasma Hydrogenation, Hydrogen Diffusion, Platelets Formation.*

NOMENCLATURE

Symbols :		**Subscripts :**	
D	diffuion coefficient, cm²/s	In	Inactive
T	temperature, °C	H	Hydrogenation
t	duration, min	MW	microwave
XE	depth, µm		
P	power, W		
N_P	phosphorus concentration, cm^{-3}		

1. INTRODUCTION

Fabrication of efficient solar cells on silicon substrates involves gettering and passivation to mitigate deleterious effects of impurities and defects. Impurity gettering is extensively used through optimization of phosphorus-diffusion needed for n^+p junction formation. Even after the gettering processes are applied, significant concentrations of impurities and defects remain electrically active in the cell.

Therefore, most silicon solar cell manufacturers apply hydrogenation from n^+ side as a technique to passivate residual impurities and defects. However, it is accepted that the presence of n^+ phosphorus doping region can seriously hinder hydrogen diffusion through the whole of the cell and therefore could reduce the passivation effectiveness of defects [1]. However, the atomic hydrogen treatment changes the phosphorus doping profile of monocrystalline silicon because of bonding (PH) [2-6]. Since the doping profile control the electrical properties of silicon devices, it is difficult to design a hydrogenation process which can increase the passivation of the defects and then improve the performance of the semiconductor devices. Thus, a good passivation is only possible if hydrogenation effects on doping is understood and appropriately accounted.

Atomic hydrogen introduced into silicon leads to a deactivation of phosphorus shallow donor due to the formation of an electrically neutral donor-hydrogen complex (PH) [2-6]. This conclusion has been well established from capacitance-voltage measurements in terms of the change in apparent phosphorus concentration before and after hydrogenation [7, 8]. Since it is generally accepted that H^- is the dominant charge state for hydrogen in n-type material, in this paper we report that neutral hydrogen H^0 can play a significant role in hydrogen diffusion and therefore in phosphorus deactivation.

In this work, the principal motivation is to study the phosphorus deactivation mechanisms in schottky diodes based silicon due to hydrogenation by microwave plasma discharge involving an electron cyclotron resonance system (MW-ECR).Different operating parameters, such as phosphorus concentration of the samples and the microwave plasma power (P_{MW}) were varied at a fixed hydrogen flux of 30 sccm. The dopant activation/deactivation in schottky diodes was monitored via capacitance-voltage (C-V) measurements by analyzing the change in apparent phosphorus concentration before and after hydrogenation.

2. EXPERIMENTAL METHOD

Hydrogenation experiments were carried out using MW-ECR plasma system (Roth & Rau) at 'Institut d'Electronique du Solide et des Système- (InESS)', Strasbourg, France. A schematic of such system has been shown elsewhere [9]. Hydrogen gas was excited by 2.45GHz microwave in a resonant chamber, where a magnetic field is applied to maintain the ECR condition. The gas pressure of plasma was 0.6 Pa at a hydrogen flux (H_2) of 30 sccm and the hydrogenation time of 60 min. The microwave plasma power (P_{MW}) and hydrogenation (substrate) temperature were varied from 100 W to 650W and 50°C to 500°C, respectively. In all cases, the input MW power and the reflection (<5%) were monitored. In order to avoid out- diffusion of hydrogen during the cool-down phase, the plasma was maintained for ~ 10 to 20 min until the substrate temperature reached to 280°C. The substrates used in this work are uniformly phosphorus doped [100]-oriented float-zone grown monocrystalline silicon (FZ-Si) wafers with different concentrations, 280µm thick and 1cm×1cm in size. Prior to hydrogenation all the silicon wafers were degreased using trichloroethylene (TCE), acetone, and methanol, treated in dilute hydrofluoric (HF) acid for removal of native oxide, then rinsed in running deionised water and finally dried into nitrogen flux. The wafers were then hydrogenated in MW-ECR plasma system. Gold contacts of 1 mm diameter were deposited using a shadow metal mask onto the hydrogenated surface, while aluminium was deposited onto the rear face to provide an ohmic contact. Then, the schottky diode was characterized by capacitance-voltage (C–V) measurements at 1 MHz and room temperature using a digital Hewlett Packard LCR meter controlled by a computer. The active donor concentration profile was extracted from these C–V measurements.

3. RESULTS

The purpose of this work is to study the phosphorus deactivation in schottky diodes based silicon due to MW-ECR plasma hydrogenation. To do this, we systematically investigate the change in the phosphorus doping profile due to the PH formation as a function of different operating conditions of hydrogenation process.

3.1. PHOSPHORUS DEACTIVATION DEPENDENT ON THE INITIAL PHOSPHORUS CONCENTRATION

The electrically active phosphorus profiles of hydrogenated samples with starting concentrations ranging from 4×10^{13} to 2×10^{15} cm^{-3} are shown in figure 1 at a fixed microwave power, hydrogenation temperature and process duration. The uniform concentrations of phosphorus in the non-hydrogenated control samples are also shown. The data reveal that increasing the initial phosphorus concentration N_P of the samples leads to a decrease in the hydrogen-phosphorus diffusion fronts XE, representing the deep diffusion of hydrogen atoms in the bulk silicon with ($1/N_P$). We find that XE = 0.75, 1.25, 3.68 and 9.93µm for N_P = 2×10^{15}, 7×10^{14}, 2×10^{14} and $4\times10^{13}cm^{-3}$, respectively. Also, the deactivation depth increased with the decreased of the initial phosphorus concentration. Consequently, our results signify the existence of a hinder diffusion of hydrogen in our samples.

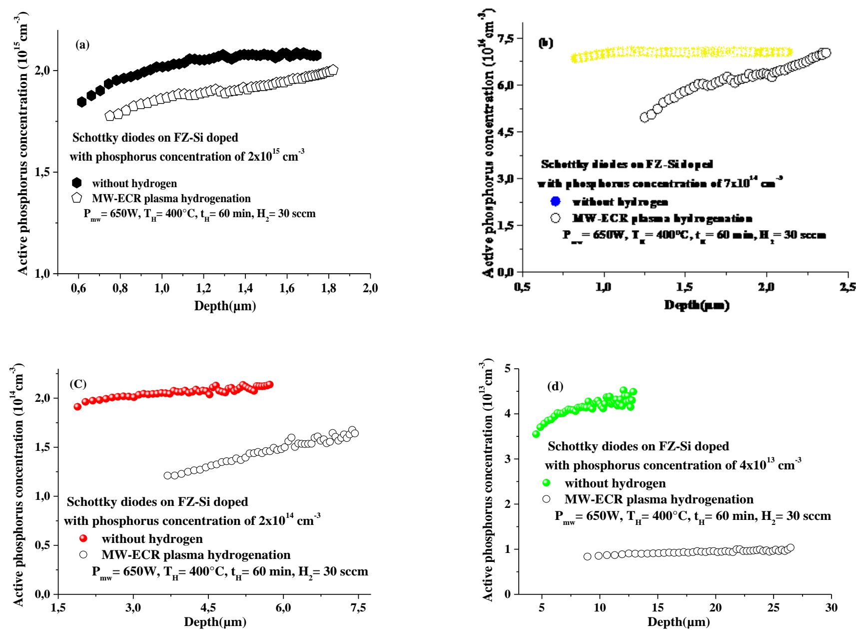

FIGURE 1. Active donor concentration profiles of hydrogenated of samples with different phosphorus concentrations N_P: (a) 2×10^{15}, (b) 7×10^{14},(c) 2×10^{14} and (d) 4×10^{13} cm^{-3}. The hydrogenation was carried out at 650W and 400°C for 60 min.

Although we did not examine the plasma content in our MW-ECR system, it is expected that H^+ is a dominant species in the hydrogen plasma [10]. The incident ions H^+ impinging the sample surface in contact with plasma are usually caused by the divergent magnetic field and the sheath potential

originating from the differences in ion and electron velocities [11]. However, According to Johnson [12], the charge state of hydrogen (H^+, H^- and H^0) in silicon depends on the Fermi level position in the band gap. It is also assumed that near and above room temperature charge change, $H^+ \leftrightarrow H^-$, occurs through the state configuration of H^0 [12, 13]. In addition, it was reported that H^0 can capture an electron or another H^0 to give respectively H^- or H_2 [14]. Although, H^0 and H^- have an extremely high diffusion coefficients in n-type silicon, hydrogen can be trapped in silicon by other hydrogen atoms resulting in the formation of hydrogen molecules, H_2, located in the subsurface layer as platelets [2, 15-17]. Because platelet nucleation occurs at phosphors sites, the increasing of phosphorus content in silicon enhances monotonically the platelet concentration [18]. Also, Huang has reported the dependence of the hydrogen diffusivity upon the average size of the platelets and suggests that the in-diffusion of hydrogen is suppressed by the platelets [19]. Consequently, H^+ absorb an electron at the sample surface to become H^0 ($H^+ + e^- \rightarrow H^0$) and the H^0 would be ionized by capturing a free electron ($H^0 + e^- \rightarrow H^-$) and then phosphorus deactivation would progress with $H^- + P^+ \rightarrow PH$. When phosphorus concentration increases, the densities of H^0 and H^- become important. This resulted in high amounts in phosphorus deactivation and larger dimension of platelets. So, the platelets impede the deep diffusion of hydrogen into the samples. However, decreasing the phosphorus concentration induces a low amount of H^- and probably a dispersion of H^0 on the sample surface. Therefore, the platelets amount will be little, which allows diffusion of both species H^- and H^0 as well as a deep phosphorus deactivation in silicon. To prove our arguments, we calculated the diffusion coefficients in our samples corresponding to depth XE through the relationship $XE = (D_H \times t_H)^{0.5}$ where D_H and t_H are the diffusion coefficient and the hydrogenation duration, respectively. The results are listed in table 1. As already mentioned above, one observes that high hydrogen diffusion coefficient is obtained for samples with low phosphorus concentration which confirm a deep penetration of hydrogen in our silicon films recorded by C-V measurements. While these values of D_H are one order of magnitude greater than those reported in the literature [20], their evolution agrees with some of the corresponding ones reported in the literature [19].

Phosphorus concentration N_P (atoms.cm^{-3})	XE (µm)	D_H (cm^2/s)
2×10^{15}	**0.75**	**1.56×10^{-12}**
7×10^{14}	**1.25**	**4.34×10^{-12}**
2×10^{14}	**3.68**	**2.7×10^{-11}**
4×10^{13}	**9.93**	**2.74×10^{-10}**

TABLE 1. Calculated of hydrogen diffusion coefficients in [100]-oriented float-zone grown monocrystalline silicon (FZ-Si) wafers with different phosphorus concentrations.

3.2. PHOSPHORUS DEACTIVATION DEPENDENT ON MW PLASMA POWER

In this section, the influence of MW plasma power, P_{MW}, which was varied from 100 to 650W, on phosphorus deactivation was analyzed at the process temperature of 400°C for 1 hour. Figure 2 shows the C–V depth profiles of the active phosphorus concentration in FZ-Si schottky diodes at various MW plasma powers. For the P_{MW} of 150 W, the deactivation of phosphorus extends to a depth of ~2.8 µm and ~45% of the phosphorus is deactivated at the edge of the hydrogen-phosphorus diffusion fronts XE. The deactivation depth and deactivated dopant density are more pronounced with the decrease of P_{MW}, representing the deep diffusion of hydrogen atoms in to the bulk silicon with inversely of MW plasma power. To further illustrate the effect of P_{MW} on phosphorus deactivation, the inactive phosphorus concentration (N_{PIn}) measured at a depth of 1.6

µm is plotted as a function of MW-ECR plasma power, as shown in figure 3. It can be seen that NP_{In} decreases with an increase in microwave plasma power and is almost linear. The existence of suppressing of diffusion process is possibly due to the increasing of the platelets density and the thickness of the subsurface region containing platelets with MW plasma power.

On the basis of results given in the literature, the MW-ECR plasma is well known by the increasing in hydrogen H^+ ions on the silicon surface when the power of microwave discharge enhances [11]. Also, the rates formations of $H^0 \rightarrow H^+ + e^-$ are very fast compared with the corresponding rates for $H^- \rightarrow H^0 + e^-$ [21]. In this case, the density of H^0 becomes high, which favours the formation of molecular hydrogen ($H^0 + H^0 \rightarrow H_2$) as platelets instead of a negative ion H^-. Accordingly, high microwave plasma power gives rise to small deactivation depths and low deactivation densities. However, decreasing the MW plasma power induces a low amount of H^+ on the sample surface. Under this situation, the probability of finding two neutral hydrogen atoms close to each other is low. This encourages the formation of H^- and the diffusion of hydrogen in depth of silicon to form phosphorus-hydrogen complexes.

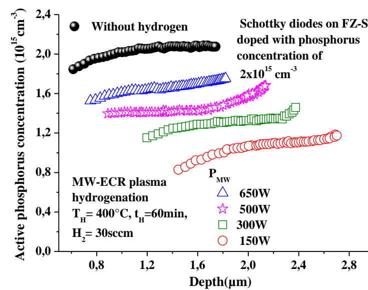

FIGURE 2. Active donor concentration profiles versus depletion depth in schottky junction diodes for various MW plasma power. The other hydrogenation parameters are also indicated.

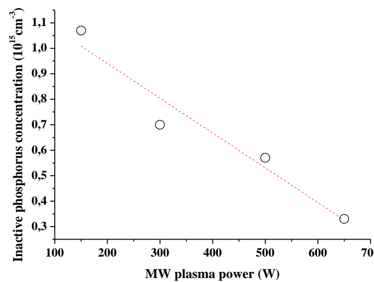

FIGURE 3. Inactive phosphorus concentration at a depth of 1.6 µm as a function of MW plasma power.

4. CONCLUSIONS

Here we have tried to study the phosphorus deactivation in schottky diodes based silicon due to hydrogenation by microwave plasma discharge involving an electron cyclotron resonance system (MW-ECR). First, we demonstrate that C-V measurement is an efficient method which can give correctly the electrically active phosphorus profile in silicon. Our results demonstrate that hydrogen deactivates the phosphorus dopant in schottky diodes to a depth which increases with the resistivity of the starting material. This behaviour understood by the formation of molecular hydrogen below the silicon surface called platelets which increase with increasing the initial phosphorus concentration. Therefore, the increase of the average platelets size decreases the density of atomic

hydrogen and in turn lowers the effective hydrogen diffusivity. The MW plasma power reveal that PH density and deactivation depth are more significant at P_{MW} = 150W. The increasing of MW plasma discharge indicates the existence of suppressing hydrogen diffusion process. It is possibly due to the increasing of the platelets density and the thickness of the subsurface region containing platelets with MW plasma power.

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