Title	触媒反応により生成されるラジカルを用いたSiへの低温の不純物ドーピング法の研究
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A Novel Method for Low-Temperature Doping to Silicon by Using Catalytically Generated Radicals

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Background of Research:

Recent trends for shrinkage of MOSFET dimension require ultra-shallow junction in a few nm scale. Novel thin doping methods using surface reaction between dopant atoms and silicon (Si) substrate are proposed to overcome the limit of ion implantation technique [1]. However, some of these methods require ultra high vacuum equipments. Thus, the development of simple doping method, applicable to mass production, is desired. In the present research, a novel doping method using the reaction between dopant radicals and hydrogen (H)-terminated Si wafer is proposed. The idea of doping using dopant radicals has been reported. In such a report, nitrogen (N) radicals are generated by plasma decomposition of source N_2 gas and radicals are incorporated as dopants in ZnTe (zinc telluride) during crystal growth of it. In contrary, the radicals generated by catalytic cracking reactions of dopant gases are used in the present research and the doping is carried out on non-growing silicon (Si) surface at temperatures lower than 350 ^{o}C.

Purpose of Research:

In this research, the radical doping conditions are explored widely and attempted to make the mechanism of radical doping clear. Using radical species generated from PH_3 or B_2H_6, the thin doping is attempted on the H-terminated Si surface at low temperatures.

Experimental procedure:

Radical species were generated in a catalytic chemical vapor deposition (Cat-CVD) apparatus by catalytic cracking reactions with heated catalyzer. PH_3 or B_2H_6 dopant gas was decomposed by the heated tungsten (W) catalyzer and the Si substrate was exposed to such decomposed radicals. Phosphorous (P) radical were generated from He diluted PH_3 (2.25%) at the catalyzer temperature (T_c) of 1300 ^{o}C. All radical doping experiments were performed at a pressure of 1 Pa. The samples were exposed to radicals and doped for 60-3600 s at the substrate temperatures (T_s) of 20-350 ^{o}C. The chamber walls were coated with an 80-nm-thick SiN_x film, which is hardly etched by atomic H and has small impurity diffusion coefficient, not to be affected by previous radical doping conditions. Hall elements were fabricated on the high resistivity counter doped substrate (>1000 Ωcm) to insulate the radical doped layer from the substrate by pn-junction. The 9-nm-thick intrinsic a-Si layer was deposited on the sample to encapsulate its surface and to measure sheet carrier concentration correctly by separating doped layer from the surface. (100) and (111)-oriented wafers were used for the substrates. The distribution of dopant atoms was investigated by secondary ion mass spectrometry (SIMS). A 60nm-thick intrinsic a-Si cover layer was formed on the radical doped surface not to be polluted in air.

Results:

Figures 1 and 2 show the sheet carrier concentration in the radical doped layer on Si (100) and (111) surface, respectively. In the case of impurity diffusion with constant surface concentration, the sheet carrier concentration should increase with proportion to square root of the diffusion time. However, the increase of the sheet carrier concentration is much smaller than the square root of the diffusion time. The carrier concentration increases with substrate temperatures.

Figure 3 shows the depth profiles of P atoms in the (100)-oriented wafer doped at the substrate temperatures of 80, 350 ^{o}C and for 60, 3600 s. The distribution of P atoms is evaluated from the depth where P atoms concentration decreases to 1/10 of peak concentration. In all samples, P atoms exist within 4-nm depth from c-Si surface. The depth distribution of P atoms is not varied by the substrate temperatures or the radical exposure times. Compared to the sheet carrier concentration, 0.2-3.6% of P atoms act as the donors. The activated ratio of P atoms increases with the substrate temperatures and does not depend on the radical exposure time. The total amount of P atoms in the sample doped at 350 ^{o}C for 3600 s is $3.6 *10^{14} cm^{-2}$

and 1.3 times higher than that of the sample doped for 60s. In all samples, the maximum amount of P atoms is around $8*10^{14}cm^{-2}$.

In the doctoral thesis, we report the formation of back surface field of a-Si (amorphous Si)/ c-Si (crystalline Si) hetero–interface by the radical doping method. The a-Si/ c-Si hetero–interface degrades severely by thermal damage. The BSF layer formation by radical doping at the low substrate temperatures from 80 to 350 °C can reduce the surface recombination at the a-Si/ c-Si interface. We also report that the possibility of p-type doping using the radicals generated from B_2H_6.

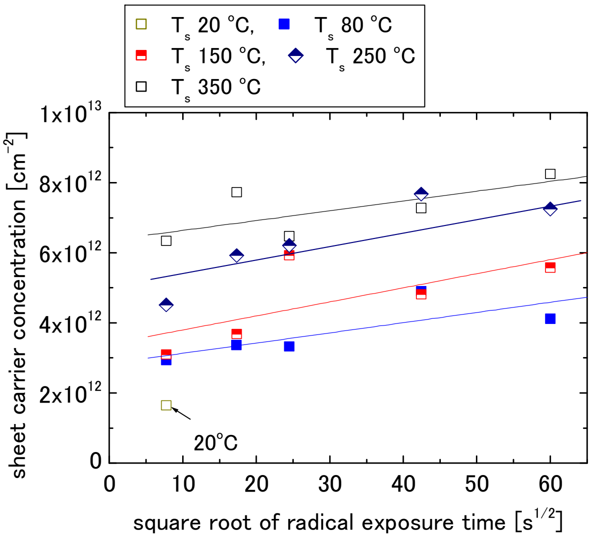

Fig.1: Sheet carrier concentration measured by Hall effect in radical doped layer on Si (100) surface. Effect of substrate temperature and radical exposure time is investigated.

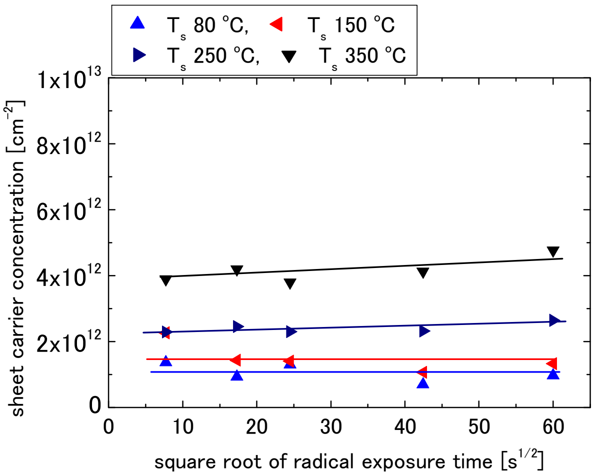

Fig.2: Sheet carrier concentration measured by Hall effect in radical doped layer on Si (111) surface. Effect of substrate temperature and radical exposure time is investigated.

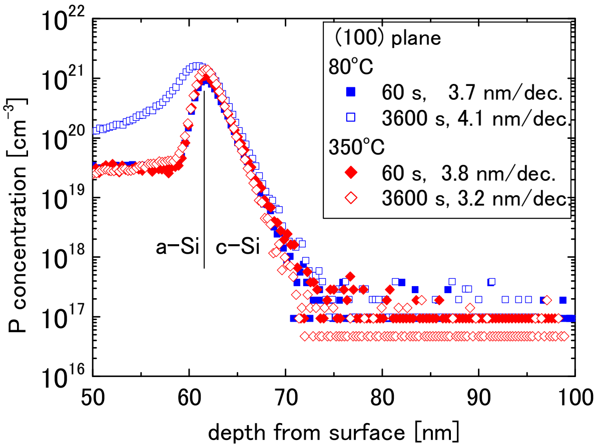

Fig.3: P atoms distribution measured by SIMS in radical doped layer on Si (100) surface. Effect of substrate temperature and radical exposure time is investigated.

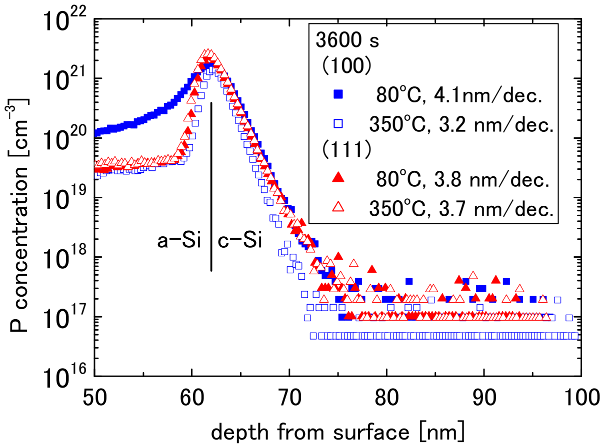

Fig.4: P atoms distribution measured by SIMS in radical doped layer on Si (100) and (111) surface.

Discussions:

The P atoms doping is performed by the reaction of radical species generated from PH_3, since PH_3 does not decompose on the Si substrate surface at the temperature range of 20-350 °C. In the case of thermal diffusion of dopant atoms, the sample doped for 3600 s expected to have 7.7 times broader distribution than that of the sample doped for 60 s, and the sampled doped at 350 °C expected to have $2.1*10^{11}$ times broader distribution than that of the sample doped at 80 °C using the activation energy of 3.66 eV of P atoms diffusion. In contrast to the expectations, P atoms distribution does not change at all and always stay within 4-nm-depth from the Si surface. This shallow and invariant P atoms distribution suggests that the P atoms distribution is due to the resolution limit of SIMS system and P atoms do not diffuse into the Si but act as the donors. This result corresponds that the extrapolated diffusion length of 80-350 °C is less than 0.5 nm of Si lattice. The amount of P atoms in the sample does not increase with the radical exposure time. The saturation of P atoms concentration is possibly related to the limit of chemical adsorption site in 1 monolayer ($6.8\text{-}7.7*10^{14}$ cm^{-2}) for P atoms. The low percentage of activated P donors is possibly due to the bond formation of P atoms on Si. Some of P atoms bonded H atoms on Si surface and the P atoms are considered not to act as donors. The present experimental results strongly imply that the doping mechanism is completely different from the doping due to the thermal diffusion but based on surface-reaction controlled ones.

Conclusions

From the above experiments and discussions, the follows are concluded:

1) By using radicals generated by catalytic cracking reaction of PH_3 or B_2H_6, the P or B atoms can dope on crystalline Si surface at the substrate temperatures of 80 to 350 ^{o}C, and the P or B atoms can act as donors or accepters without annealing.
2) The doping mechanism appears completely different from the doping by thermal diffusion of impurities, but appears to be related with surface reaction of dopant radicals.
3) This low temperature doping technique can be applied for the doping of back surface field in Si solar cells.

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