MODERN AND LOW-COST TECHNOLOGY WITH RAPID PHOTOTHERMAL PROCESSING FOR SILICON SOLAR CELLS FABRICATION

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Abstract

The modern and inexpensive Nonconventional Technology with Rapid Photothermal Processing (RPP) and Rapid Thermal Processing (RTP) presents an important direction in the advanced technologies for micro-nano-electronics and solar cells fabrication. The priority of this technology compared to that conventional is in rapidity of the technological processes (diffusion, implantation and oxidation), energy budget, materials and gases reduction etc. RPP provide materials with homogenous microstructures, higher performance, higher reliability and yields of semiconductor devices.

This report concern the investigations of most important steps of RPP solar cells fabrication: enhanced diffusion of P and B in silicon, Zn in GaAs and physic-mathematic model, shallow and ultra-shallow n^+- p and n^+- p – p^+ junctions in Si, GaAs, and ohmic contacts.

Key words: Rapid Photothermal Processing; enhanced diffusion; solar cell.

1. INTRODUCTION

The modern and low-cost Nonconventional Technology with Rapid Photothermal Processing (RPP) and Rapid Thermal Processing (RTP) are appreciated by many publications and RTP International Conferences. The milestones and priority of this technology compared to that conventional is in rapidity of more than 10-100 times of the technologic processes (diffusion, implantation and oxidation), in the energetic budget reducing up to 10-100 times, in the essential economy of materials, gases etc. RPP provide materials with homogenous microstructures, higher performance, higher reliability and yields of semiconductor devices. This Technology will change radically the concept of production in micro – nanoelectronics: individual processing of wafers with unlimited diameter (at present 300mm); thus opening the way to an all rapid- photothermal process for solar cells and other devices fabrication. RPP directly addresses the issue of fabrication cost by reducing the processing time, temperature and energy in comparison with conventional furnace processing without significant loss in the solar cells performance.

In the late 70's, integrated circuit researchers investigated several thermal – processing technology as on alternative of conventional furnace processing named Rapid Thermal Annealing (RTA), or Rapid Thermal Treatment (RTT) or RTP. In 1985 - 2005 Prof. R. Singh and his colleagues have published more than 250 papers and 10 books concerning physical and technological base of RTP and RPP technology; for the first time have been demonstrated the priority of RTP – technology compare to conventional furnace (CF) technology [1,2] - fast heating and cooling rate, the role of photo–spectrum in RTP, recommendation of RTP as commercial technology in microelectronics and special for Solar Cells fabrication [3,4]. At the same time (1985 - 2005) Prof. T. Shishiyanu and his colleagues demonstrated that by Pulse Photon Annealing is possible to improve the characteristics and quality of GaAs - Shottky diodes and *p-n* – junctions [5,6], to obtained the ultra- shallow and abrupt impurity profiles of Si, GaAs and InP for MESFET transistors [7], to improve the quality and reliability of GaAs - Shottky diodes, avalanche diodes and components of Si – integrated circuits [8], RPP technology of shallow *p-n* junctions for solar Cells and Sensors [9], RPP for gas sensors applications [10,11], RPP Technology, models and applications [12].

During the last years RPP Technology is very attractive for Solar Cells fabrication as Modern and Low-cost Technology recommended by R. Singh in 1985 as promising photovoltaic technology [2]. There are experimental results which demonstrated the possibility and priority of a rapid photothermal solar cell fabrication on polycrystalline silicon (poly-Si) predicted to become the most common substrate material for photovoltaic cells [1-9, 12-14]. Combination of RPP technology and poly-Si can guaranty the development and implementation of the low-cost solar cells industry.

2. THE PHYSICAL BASE OF RPP- TECHNOLOGY

The physical base of RPP- Technology is the dissociate mechanism of diffusion with simultaneous influence of thermal and quantum factors on semiconductors. The thermal factor excites the lattice phonons and quantum effects excite the electronic systems. As a result the activation energy of technological processes (diffusion, ion implantation, oxidation, chemical reaction etc.) is reduced (as process temperature and time) and diffusion coefficients are higher. According to Chiayka–Sinischuk–Shishiyanu stimulated diffusion model by RPA and radiation ($h\nu$ – light, γ, α, β, e^-, X) is possible to improve the characteristics and parameters of Shottky diodes and *p-n* junctions by SD of impurities depending on concentration of vacancies in thermodynamic equilibrium and non equilibrium, increasing temperature and diffusion coefficient [5-7]:

$$D^* = D_0\left[1+\frac{\gamma_n n}{\gamma_p p}\right]^{-1}\exp\left\{-\frac{E_D-\varepsilon_\nu}{kT}+\frac{1}{2}a\frac{h\omega}{kT_0}\left[1-\frac{T_0}{T}\right]\right\},\ T = T_0+\frac{I\alpha\varepsilon_\nu}{n\cdot l}\cdot\frac{x}{L}\left(L-x\right), \qquad (3)$$

where I – γ-radiation intensity, $D_0 = \nu\cdot d^2$; ε_ν – e^- excitation energy, α – radiation absorption; etc.

This model demonstrates that, as high is the excitation energy the higher is the enhanced diffusion coefficient, thus explaining the experimental results of SD in semiconductors (Si, GaAs, InP, GaP etc.).

3. EXPERIMENTAL RESULTS AND DISCUSSION

In our experiments was used the RPP system with temperature range (200-1200°C), heating rate (150-200°C/s) and duration 1-600 s. with halogen lamps and UV source. In fig.1 is presented the comparison of the phosphorous profiles after diffusion in Si with (1) and without UV radiation [4] in two diffusion steps: (i) CF diffusion at 840°C for 2 h in $POCl_3$ and second: (i) 950°C, 5min, $POCl_3$ furnace diffusion, (ii) glass layer removal and diffusion, (iii) RTP diffusion at 900°C for 5 min, with and without the presence of UV radiation. From this data the enhanced diffusion by UV radiation is evident; photons with wavelength between about 400 and 800nm contribute to both thermal and quantum effects. Only quantum effects are observed with photons less than 400nm [4].

Another experiment was done with one step RTP enhanced diffusion by halogen lamp system (IFO–6) where both thermal and quantum effects took place. In fig. 2 is presented the P in Si after one step RTP enhanced diffusion from PSG, (T= 900°C, t = 16s) obtained by GDOES method [13]. One can see that the shape of this profile (fig.2) is similar to profile in fig. 1, obtained by SIMS.

The experimental results of RPP - SD of P, B in Si; Zn in GaAs are presented in Tab.1, 2, 3.

The comparison of estimated from Table 1 – 2 parameters of RPP with CS diffusion demonstrate: (i) RPP enhanced diffusion coefficient is higher by 2-3 orders, (ii) activation energy decreased for B from

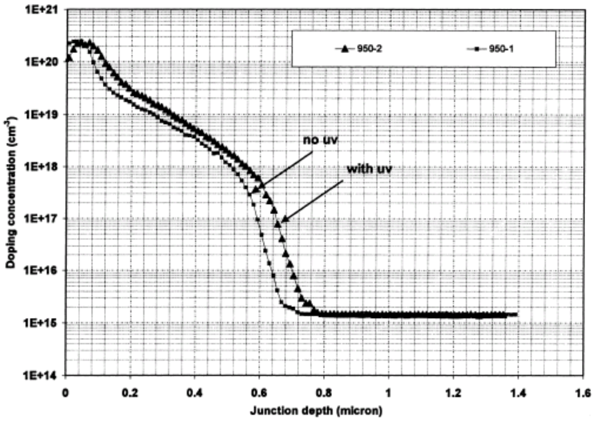

Fig. 1. Comparison of the results with and without the presence of UV radiation [4].

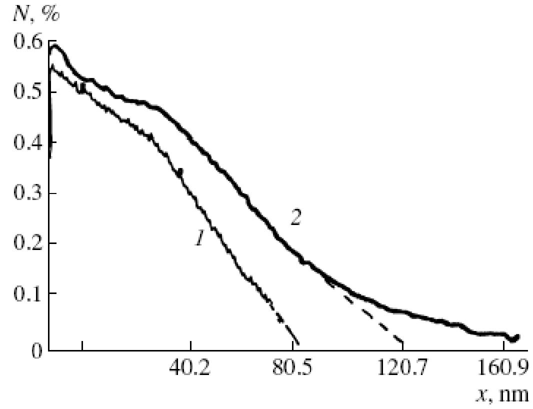

Fig. 2. Concentration profiles of P in Si after stimulated diffusion under RPP for 16 s at 900°C (*1*) and1000°C (*2*) [9].

Tab. 1. Enhanced photon diffusion of P in Si.

T, °C	460	700	1000	1080	1120	1200	1250
t, sec	4	6	8	10	12	14	16
x,μm	0.14	0.2	0.25	0.3	0.38	0.46	0.54

Tab. 2. Enhanced photon diffusion of B in Si.

T, °C	400	500	700	1080	1120	1200	1250
t, sec	2	4	6	10	12	14	16
x, μm	0.13	0.18	0.2	0.32	0.36	0.4	0.51

Tab. 3. Enhanced photon diffusion parameters of Zn in GaAs.

T, ^{0}C	T, K	t, sec	l (μm)	R/ •	D, cm^2/s	E	Comments
520	793	5	0.21	-	$2.9\text{x}10^{-10}$	$N > 10^{20}$cm^{-3} $E \approx 1$eV	$N(x,t) \neq$ erf Z, erfcZ.
640	913	7	0.27	1015	$3.5\text{x}10^{-10}$		
760	1033	9	0.34	960	$4.3\text{x}10^{-10}$		
780	1053	10	0.37	415	$1.2\text{x}10^{-10}$	$N < 10^{20}$cm^{-3} $E \leq 2$eV	$X \sim \sqrt{t}$
900	1181	15	0.64	210	$1.4\text{x}10^{-9}$		
950	1223	17	0.73	190	$1.1\text{x}10^{-9}$		

enhanced diffusion coefficient is from $2.9\text{x}10^{-10}$ to $1.1\text{x}10^{-9}$, activation energy $E \approx 1$eV at ($N > 10^{20}$cm^{-3}) and $E \leq 2$eV at $N < 10^{20}$cm^{-3}. The CF diffusion coefficient of Zn in GaAs ($N < 10^{20}$cm^{-3}) is about 10^{-14} –10^{-11} cm^2/s at 600-950°C and activation energy 2.5 eV. These experimental results shown that by RPP – enhanced diffusion in 5 –20 sec is possible to obtain 0.1 – 0.5 μm n^+-p and p^+-n junctions, sheet resistance 5-400Ω/□ and surface concentrations about 10^{18}- 10^{21}cm^{-3}.

Is important to mention that efficiency of quantum enhanced diffusion is higher at the beginning (initial step) of RPP at the surface and in ultra- shallow and shallow layer of the samples in non thermodynamic equilibrium of excited atoms and vacancies. At the next step of photothermal processing the quantum effect have smaller influence on diffusion. This can be motivated by absorption of higher energy quantum at surface of semiconductor and thermodynamic equilibrium of vacancies and other lattice defects in semiconductors. The competitiveness of the solar cells technology in energy production is strongly dependent on its price. RPP directly addresses the issue of fabrication cost by reducing the processing time, temperature and energy in comparison with CF processing without significant loss in the solar cells performance. RPP reduced the microscopic defects leading to higher performance and better reliability and yield.

The most important is that by RPP technology is possible to realize all steps of the solar cell fabrication: wafer pre-treatment, simultaneous formation of emitter by phosphorous diffusion, base field and ohmic contacts by (Al,Pd,Ag,Ni,Cu)-diffusion, antireflection coating; front side metallization.

The importance of simultaneous enhanced diffusion of P and Al is in acceleration of P diffusion, lattice defects reduction and improvement of electrons and holes lifetimes. By RPP technology is possible to prepare higher reliability ultra shallow p-n junctions and ohmic contacts for solar cells.

4. CONCLUSIONS

In this paper is confirmed the role of thermal and quantum effects in RPP enhanced diffusion of P and B in Si, Zn in GaAs. The physical base of the enhanced diffusion is the dissociate mechanism of interstitial, substitutional atoms and vacancies. Experimentally have been demonstrated that the simultaneous influence of thermal and quantum effects lead to reducing the activation energy, increasing of diffusion coefficient and decreases the processing time (for P, B in Si and Zn in GaAs) in accordance with physic – mathematics models. The most important is that by RPP technology is possible to realize all steps of the solar cell fabrication: wafer pre-treatment, simultaneous formation of emitter by phosphorous diffusion, base field $n^+ - p$, *and* $n^+ - p - p^+$ and ohmic contacts by Al - diffusion, antireflection coating and front side metallization. The priority of RPP technology for solar cells fabrication is the energy and fabrication time reduction.

REFERENCES

1. R. Singh et al. “Role of photoeffect in RTP”, Journal Electronics, v.58, 1985, p.19.
2. R. Singh. RTP as promising photovoltaic technology, 1985 Electrochemical Society meeting.
3. R. Singh. Rapid Thermal and Related Processing Technique, Book Edit by Int. Soc. of Optical Eng., 1991, vol. 1393, pp. 1-422.
4. R. Singh et al. Rapid Photothermal Processing in semiconductor manufacturing technology for the 21st Century, Applied Surface Science 168, 2000, 198-203.
9. T.S. Shishiyanu et al. Radiation–enhanced diffusion in metal-semiconductor contacts. Physics and Technique of Semiconductors (in Russian), № 4, 1985, 674-677.
10. T.S. Shishiyanu et al. Application of pulse photon annealing for semiconductor structures treatment. In Review: Ternary semiconductors and applications, Edit by Stiinta, Chisinau, 1987, p.215.
11. T.S. Shishiyanu. The formation of semiconductor Device properties by stimulated diffusion in semiconductors. Invited paper. III Inter. Workshop on Semiconductor Devices, NewDelhi, India, 1991.
12. T.S. Shishiyanu, I.K. Sinischuk, S. Shishiyanu. The improvement of quality and reliability of integrated circuit compounds by pulse photon annealing and stimulated diffusion in semiconductors, International Journal Electronics, v. 78, №4, 1996, 699-706.
13. S. Shishiyanu, T. Shishiyanu, S. Railean. Shallow p-n junction formed in silicon using pulsed photon annealing, Physics and Technique of Semiconductors (in rus.) Vol. 36, №. 5, 2002, 611–617.
14. Sergiu T. Shishiyanu et al. Sensing characteristics of tin-doped ZnO thin films as NO_2 gas sensor, Sensors and Actuators B 107, 2005, 379-386.
16. Sergiu T. Shishiyanu et al. Photoluminescence of chemical bath deposited ZnO:Al films subjected to rapid thermal annealing, Thin Solid Films, Accepted, In Press, Available online - May 2005.
17. Sergiu T. Shishiyanu. Nonconventional technology in microelectronics with photon annealing and stimulated diffusion, Book Edit by Tehnica, Chişinău, 1998, pp. 1-221.
18. S.T. Şişianu. GDOES investigations of shallow junctions in Si, GaAs, InP obtained by photonic treatment and stimulated diffusion. Report on Scientific-Practical Conference Advanced Technologies in XXI Century, Academy of Sciences of Moldova, Edit by Ştiinţa, Chişinău, 2000.
20. S. Bourdais et al. Comparative study of rapid and classical thermal phosphorus diffusion on polycrystalline silicon thin films, J. Solar Energy Materials and Solar Cells 65 (2001) 487-493.