DOI: https://doi.org/10.54966/jreen.v3i1.908 *Rev. Energ. Ren. Vol.3 (2000) 29-38*

Electrically Active Defects in Silicon after various Optical Thermal Processing

Abdelfettah Barhdadi [1,2] and Jean Claude Muller [3]

[1]Laboratoire de Physique des Semiconduteurs et de l'Energie Solaire (P.S.E.S.), Ecole Normale Supérieure, P.O. Box: 5118, Rabat-10000 (Morocco)

[2]The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy.

[3]Laboratoire PHASE, UPR 292 du CNRS-SPI ., P.O. Box: 20 CR, F-67037 Strasbourg Cedex 2, FRANCE

Abstract – *Schottky diodes have been made on virgin n-type monocrystalline silicon annealed by various optical thermal processes including lasers and incoherent light heat-pulses. The electrical characteristics of the diodes have been measured as a function of the laser energy density. A strong change in all their electrical parameters occurs for energy density equal or higher than a fluence threshold at which the processed silicon surface layer turns into melt. Capacitance measurements and DLTS analyses show that laser irradiations introduce a large density of deep levels related to donor defects in the processed surface region. DLTS analyses performed on samples processed with incoherent light heat-pulses show that deep levels related to majority carrier trap defects are also generated by this new thermal process. The results have been compared to those obtained from parallel analyses carried out on p-type silicon processed using either rapid or conventional thermal annealing mode.*

Résumé – *Des diodes Schottky sont réalisées sur du silicium monocristallin de type n après des traitements thermiques optiques par laser pulsé ou par impulsions lumineuses en "flash". Les caractéristiques électriques de ces diodes sont mesurées en fonction de la densité d'énergie déposée. Leurs paramètres électriques principaux montrent une grande dégradation à partir d'une énergie seuil qui fait fondre les surfaces irradiées. Les mesures capacitives et analyses DLTS montrent la présence de plusieurs niveaux profonds associés à des centres donneurs dans les zones traitées. Ces résultats sont comparés à ceux parallèlement obtenus sur des échantillons de type p ayant subi des traitements isothermiques conventionnels ou rapides.*

Keywords: Rapid thermal processing, Pulsed laser, Schottky diode, Silicon crystal, DLTS, Defects.

1. INTRODUCTION

Optical Thermal Processes (OTP) can offer many advantages in a strategy focused on cost-effective techniques for the preparation of electronic devices, especially solar cells, in an automatic and continuous way. There exist several OTP which operate either in an adiabatic regime with coherent light (Lasers) or in an isothermal short duration regime with incoherent light (Rapid Isothermal Processes). These optical heating techniques are advantageous because they are fast and clean as only the sample is heated and not the reactor. Moreover, the lamp furnace annealing, which is presently as fashionable annealing mode, offers some attractive features such as low time and power consumption and hence a minimum overall thermal budget [1]. However, despite this great interest, one of the major obstacles to the development of OTP for large practical and industrial applications is the fact that they induce an important concentration of electrically active defects in the processed samples. These defects were throught to be frozen-in during the rapid quenching procedure characterising OTP.

In this paper we report some experimental results obtained on OTP-induced defects in silicon material used in the technology of solar cells. Three different OTP including two solid-state pulsed lasers and an incoherent light pulse heating technique have been considered. We examine their effects on the electrical properties of silicon Schottky diodes. Some of the observed effects are compared to those resulting from the conventional annealing treatments.

2. EXPERIMENTAL PROCEDURE

The investigations were carried out on virgin n-type phosphorus-doped <100> oriented float-zone growth (FZ) monocrystalline silicon of 1-5 Ω.cm resistivity. The samples were first degreased in boiling trichlorethylene for 5 min., cleaned in acetone, rinsed in running demonised water and dried with flowing nitrogen gas. After, they were chemically polished in CP4 etching mixture for 2 min., carefully rinsed again in running demonised water and finally dried under nitrogen gas flux to be ready for the optical thermal treatments. These were performed, immediately after chemical preparation of the samples, in three different manners:

1) By a Q-switched solid-state pulsed Ruby laser (λ = 694.3 nm), operating in the monomode released working regime, giving a single spot of about 9 mm in diameter and pulses of 20 ns duration. The beam energy density E ranged from 0.6 to 1.2 J/cm².
2) By a Q-switched solid-state pulsed Nd-YAG laser, operating at 530 nm wavelength. This laser delivers pulses of about 100 ns duration and a small spot diameter (typically 0.1 mm) but at a very high repetitive rate, up to 10 kHz. Large areas are covered in this case by scanning the pulsed beam under controlled over lapping conditions. The beam energy density E has been varied from 0.6 to 1.3 J/cm².
3) By a large-area incoherent lamps heat source proved to be one of the most reliable rapid thermal annealing (RTA) techniques reducing the thermal budget in electronic device processing [1]. RTA isothermal treatments were carried out in a flowing argon gas ambient, for 10 s, at temperature ranging from 450 °C to 850 °C in steps of 200 °C, using a commercial FAV4 model from JIPELEC (France) heat pulse lamp furnace. In this system the heating is produced by a ramp of quartz halogen lamps. A typical time temperature profile is composed of a rise time of about 5 s, a period of few seconds at maximum temperature, and subsequent natural ramping down at the end of the cycle with cooling rate typically around 100°C.s^{-1}. In this study, the light irradiations were performed by heating and cooling stages similar to those used in conventional furnace treatments so as to allow for a comparison with our previous results [2-4]. Some parallel light irradiations have also been performed on virgin p-type boron-doped <001> oriented Czochralski pulled (CZ) monocrystalline silicon of 20 Ω.cm resistivity, to look at the influence of the starting wafer on the obtained results.

To analyse the samples, four Schottky diodes were realised on each one of them. Next, current-voltage (I-V) and capacitance-voltage (C-V) characteristics of the diodes have been measured and their most important electrical parameters have been deduced. The induced electrically active defects generated in the bulk of the samples were investigated by DLTS.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Devices processed with pulsed laser

I-V characteristics of Schottky diodes made on Nd-YAG laser processed samples have been recorded as a function of the beam energy density E (figure 1). Schottky diodes made on reference unirradiated samples exhibit good and reproducible rectifier electrical characteristics. For low energy densities ($E \leq 0.9$ J/cm²), the I-V behaviour of a reference device remains well preserved. The rectifier effect disappears at nearly $E = 1$ J/cm². With increasing energy density up to this value, a drastic degradation occurs and the I-V curves become no longer rectifying indicating the formation of a quasi-ohmic contact. It can be noticed that I-V measurements performed at 77 K do not show the same experimental results. Indeed, for 1.3 J/cm² irradiated sample for example, I-V curves show a quasi-ohmic behaviour at 300 K, but at 77 K they are very close to that of the reference Schottky diode.

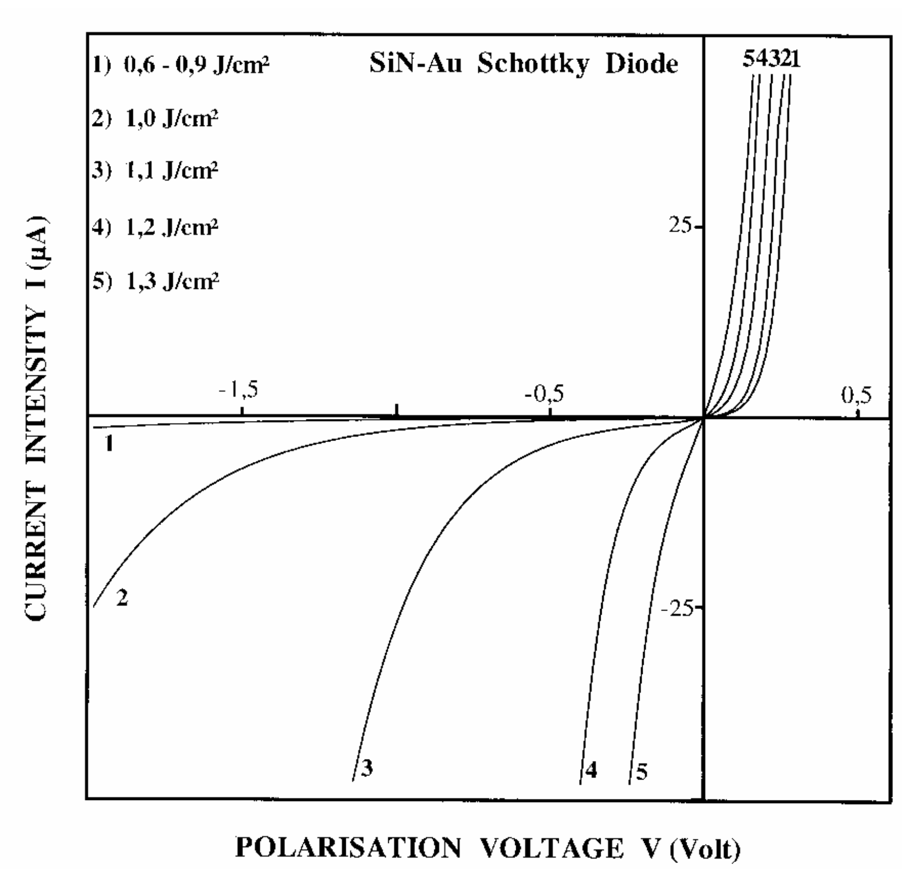

Fig. 1: Evolution of the I-V electrical characteristics of Au-Si Schottky diodes as a function of pulsed Nd-YAG laser energy density. A strong electrical degradation in I-V curves occurs at ~ 1 J/cm² threshold.

Figure 2 shows the evolution of the potential barrier height Vbn with the beam energy density E of Nd-YAG laser. Vbn has been calculated from the forward saturation current of Schottky diodes by assuming a pure thermoionic transport. Starting from a typical value of 0.75 V for the reference diode, Vbn remains practically constant for the lower energy densities ($E \leq 0.9$ J/cm²). With increasing E, Vbn decreases slightly after 1 J/cm² and goes down continuously to reach very low values (< 0.6 V) for the higher energy densities.

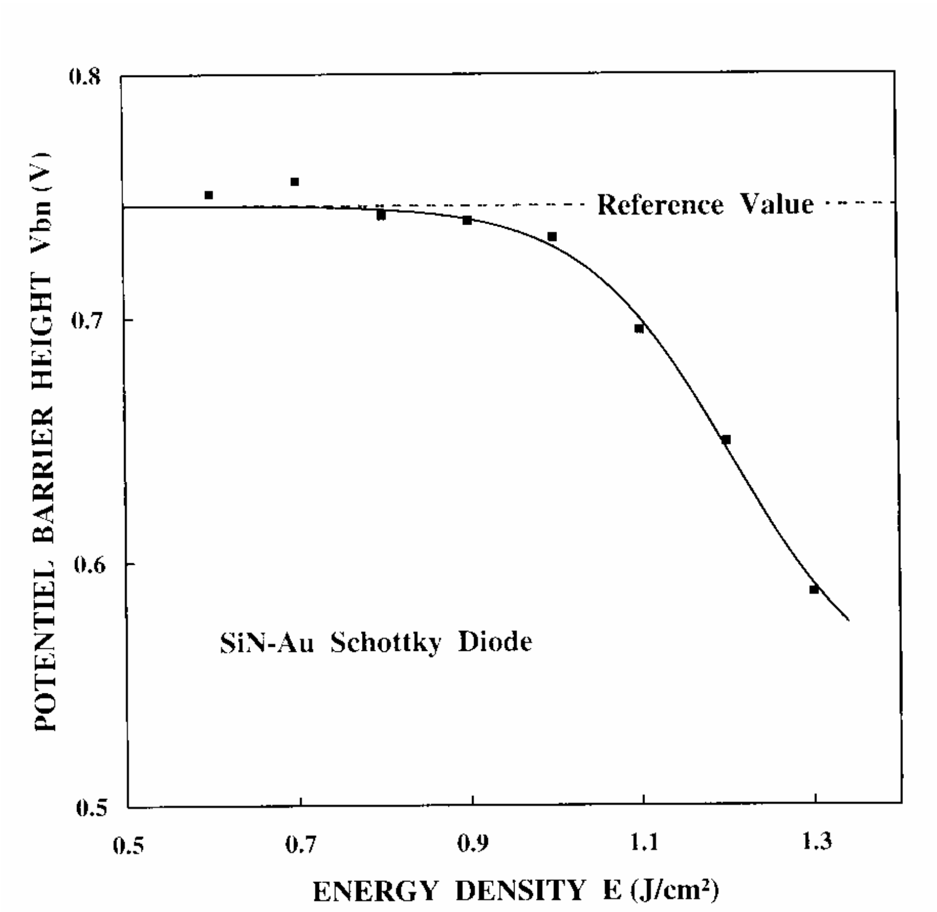

Fig. 2: Evolution of the potential barrier height Vbn of Au-Si(N) Schottky diodes as a function of pulsed Nd-YAG laser energy density. A strong electrical degradation in Vbn occurs at ~ 1 J/cm² threshold.

The change in the diode quality factor n as a function of Nd-YAG laser energy density is reported in Figure 3. Starting from a typical 1.15 value for the reference Schottky diode, n remains practically unchanged for the lower energy densities. At nearly $E = 1$ J/cm², n shows a small increase and then goes up continuously to reach values higher than 3 for $E > 1.3$ J/cm².

Capacitance-Voltage measurements have been carried out at 1 MHz frequency. Figure 4 shows the evolution of the measured diode capacity value at -0.5 V with the beam energy density E of Nd-YAG laser. Lower energy densities induce practically no change in the capacity value. Following irradiation at $E = 1$ J/cm² the capacity value starts increasing significantly and quickly becomes very high for the higher energy densities indicating an increased concentration of ionised donor centres close to the surface of the sample.

From the above results, we notice practically the same energy density threshold around 1 J/cm² for which all the electrical properties of the diodes start to degrade. Indeed, for a beam energy density lower than 1 J/cm², Nd-YAG laser produces only very small changes in the diode electrical parameters.

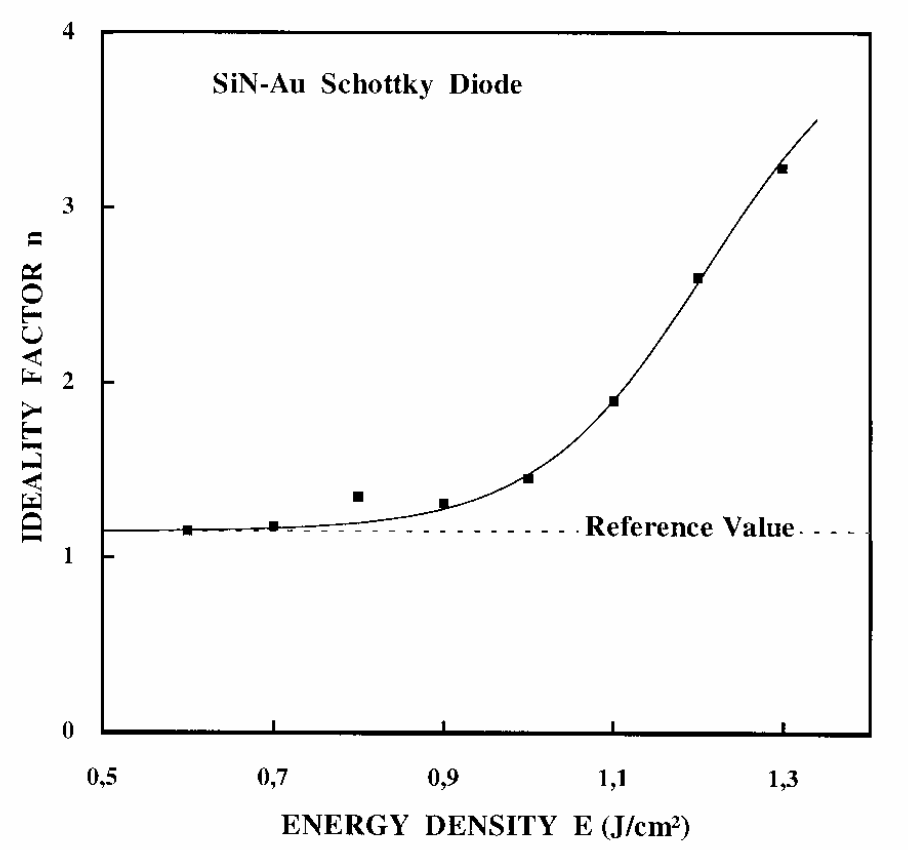

Fig. 3: Evolution of the ideality factor n of Au-Si(N) Schottky diodes as a function of pulsed Nd-YAG laser energy density. A strong electrical degradation in n occurs at ~ 1 J/cm² threshold.

However, above this threshold a fast degradation occurs and all of the diode electrical properties indicate practically the same behaviour and the coherent trends. The sharp increase of the capacity value measured at -0.5 V as well as the great difference observed between the I-V curves recorded at 77 K and at 300 K indicate that high concentration of donor centres are induced by laser irradiations in the vicinity of the processed sample surfaces. Computer simulation through our model calculation [5] have shown that, for energy density around or higher than 1 J/cm², the silicon surface processed layer turns into melt. So, we think that the most damaging defects responsible for the diode degradation are generated in the laser induced molten layer and we believe that they result from the quenching process due to the fast melt cooling and solidification rate.

The experimental procedure and study described above has been entirely and systematically carried out again in exactly the same experimental conditions but Nd-YAG laser has been substituted for pulsed Ruby one. The energy density threshold, for which a significant degradation in Schottky diode electrical characteristics and properties occurs, was about 0.7 - 0.8 J/cm². This degradation threshold coincide also with the beam energy density value for which the surface processed layer of the silicon sample turns into melt [5].

Figure 5 shows a typical DLTS spectrum from a Ruby laser-irradiated sample at 1 J/cm² beam energy density, which is higher than the melting and electrical degradation energy threshold.

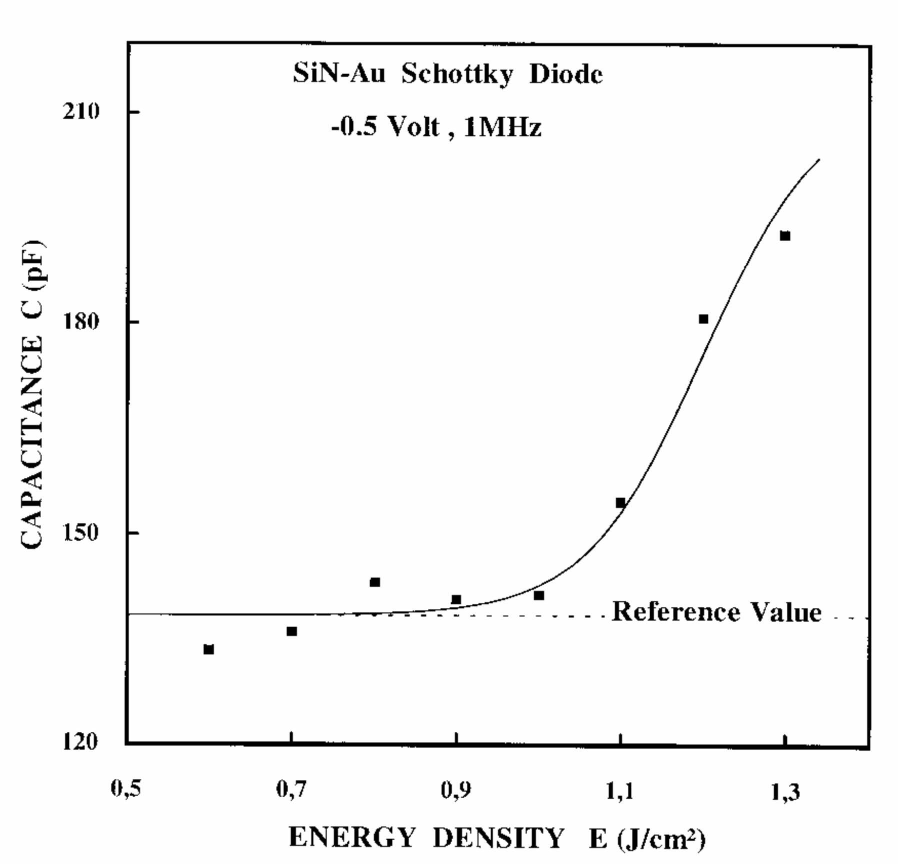

Fig. 4: Evolution of the capacitance C measured at -0.5 V of Au-Si(N) Schottky diodes as a function of pulsed Nd-YAG laser energy density. A strong increase in C (-0.5 V) value occurs at ~ 1 J/cm² threshold.

The spectrum exhibits three main peaks labelled E1, E2 and E3 due to electron traps bcated respectively at 0.32 eV, 0.43 eV and 0.58 eV below the conduction band. The corresponding capture cross sections of the traps are 4.4 10^{-16} cm², 1.4 10^{-16} cm² and 5 10^{-15} cm² respectively. The dominant defect peak in the spectrum, i.e., the Ec-0.32 eV trap, gave a concentration of about 6 10^{14} cm^{-3} at -1 V reverse bias and 50 s^{-1} emission rate.

These same deep levels have been seen also in samples irradiated with pulsed Nd-YAG laser at 1.6 J/cm² energy density, which is well above the melting and electrical degradation threshold [6]. Considering the fact that the melt depths induced in the silicon wafers by the two lasers at their corresponding energies (1 J/cm² for Ruby and 1.6 J/cm² for Nd-YAG) are approximately equal (~ 500 Å) [5], it is not surprising that the same levels are observed here. This suggests that the essential parameters in defect formation during liquid-phase processing are the melt depth and the velocity of solidification or melt cooling rate. A situation in which melt depths are equal and natural cooling is employed produces the same defects irrespective of the type of laser used. The defect states produced are characteristics of pulsed laser-treated silicon, and much tentative identification has been proposed [7-9]. In our previous works, we have showed that these defects can be electrically neutralised either by low-energy hydrogen ion implantation [10] or by rapid thermal annealing at 600°C for 60 s duration [6].

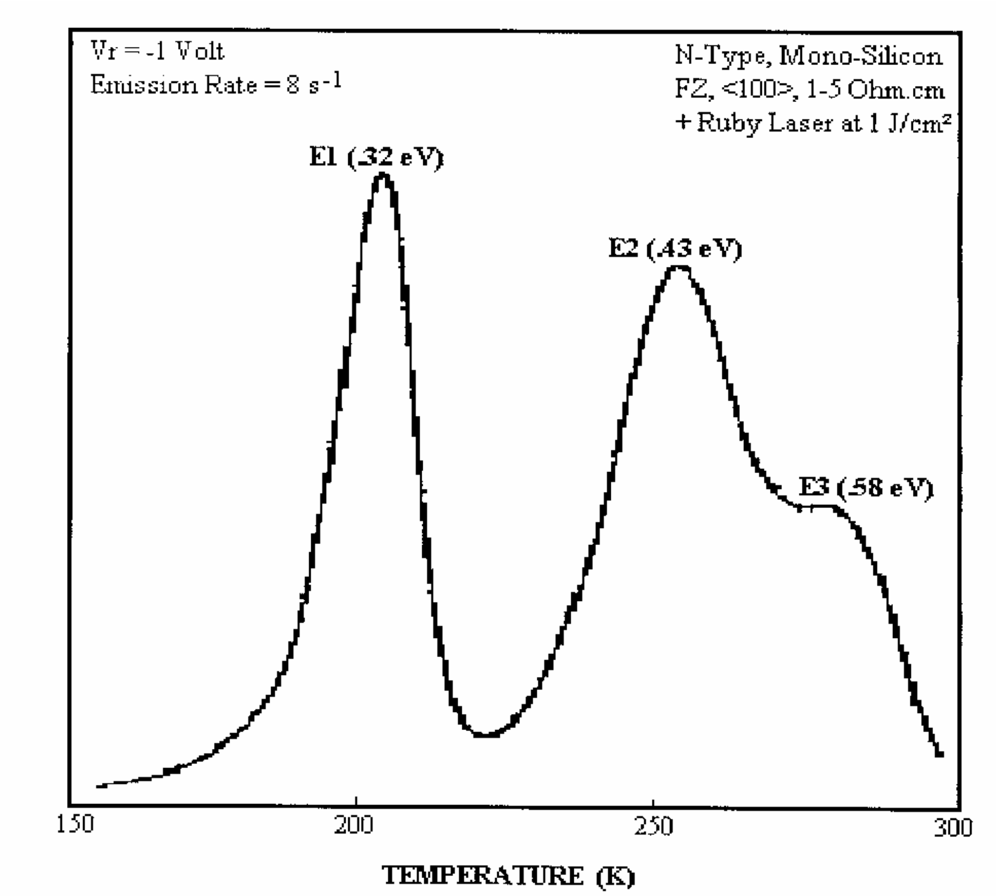

Fig. 5: D.L.T.S. spectrum from Au-Si(N) Schottky diodes after pulsed Ruby laser at 1 J/cm² beam energy density which is higher than the melting energy thershold. The spectrum exhibits three main peaks labeled E1, E2 and E3 due to electron traps located respectively at 0.32 eV, 0.43 eV and 0.58 eV below the conduction band.

3.2. Devices processed with fast thermal annealing technique

Figure 6 shows the evolution of DLTS spectrum obtained on n-type silicon samples processed in the rapid thermal furnace as a function of the annealing temperature. Curves 1 and 2 indicate that no DLTS peaks are detected in the samples processed at 450 °C or 650 °C respectively. However, at 850 °C we observe a well resolved peak (curve 3) which is associated to an electron trap deep level located at Ec-0.21 eV with an effective cross section in the order of E-17 cm². The same level has been also seen, with lower concentration, in n-type silicon samples processed for 30 min. at 850 °C in the classical thermal furnace [3,4]. The origin of this level still not clarified but, considering the experimental conditions by which it appears, we believe that external contamination is mostly responsible for its generation [3,4].

Figure 7 shows a typical DLTS spectrum from Schottky diodes realised on rapid thermal processed p-type silicon samples. At least four hole trap peaks labelled H1 to H4 can be resolved. The energies of the corresponding four deep levels are respectively 0.18 eV, 0.22 eV, 0.33 eV and 0.43 eV above the valence band. The dominant peak in the spectrum, i.e., the Ev+0.43 eV level acts as recombination centre [11].

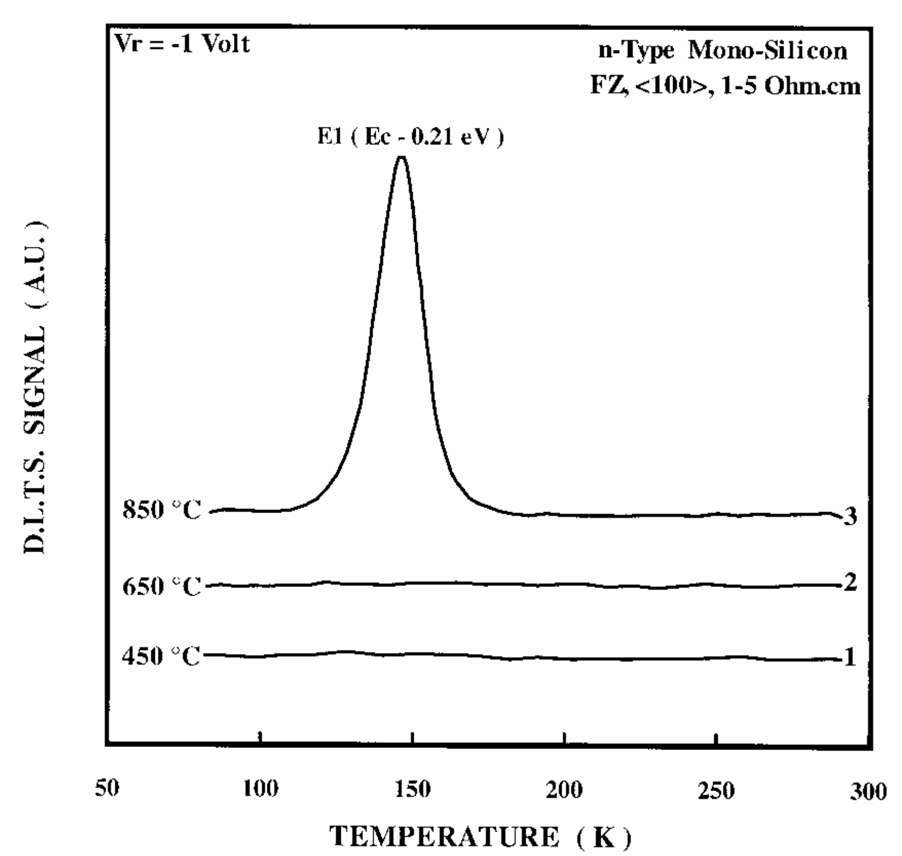

Fig. 6: D.L.T.S. spectrums from Au-Si(N) Schottky diodes after incoherent light thermal processing at different temperatures. The thermal processings have been performed under Argon atmosphere, for 10 s in Rapid Thermal Annealing Furnace.

It has previously been observed by many other authors [12-16] and attributed to interstitial iron atoms (Fe_i) resulting from the dissociation of Fe-B pairs existing at great concentration in as-grown Czochralski-pulled p-type silicon ingots. We cannot exclude the formation of complexes between vacancies created by nonequilibrium conditions during fast thermal processing and impurities such as heavy metallic atoms or oxygen and carbon which are often present at high level of concentration in CZ grown silicon [17]. So, from these considerations, the deep level located at Ev+0.33 eV may be attributed to Fe-O complex [14]. In the same way, the two other deep levels H1 and H2 are most probably connected with interstitial oxygen-vacancy (O_i-V) complex [18] and bivacany defect [19-21] respectively. Precise identification of the nature of the defects or complexes corresponding to the observed deep levels will require further investigations.

4. CONCLUSION

In summary, this work has clearly demonstrated that pulsed Nd-YAG laser-related defects are almost identical to those generated by the other solid-state pulsed Ruby laser. The electrically active defects induced by these two lasers working in the liquid-phase regime seem to be solely due to the regrowth velocity as was speculated in the past. A post-laser hydrogen ion implantation for less than one minute or a thermal treatment with incoherent light pulse technique around 600 °C for one minute allow all of these defects to anneal out. From these results it is clear that, for example, the combination of a pulsed laser for electronic device processing and of rapid thermal annealing for residual defect removing may lead to better device performance, and certainly provides a considerable reduction in processing time. Obviously, rapid thermal annealing must be done at temperatures lower than 800 °C else other electrically active defects will be produced.

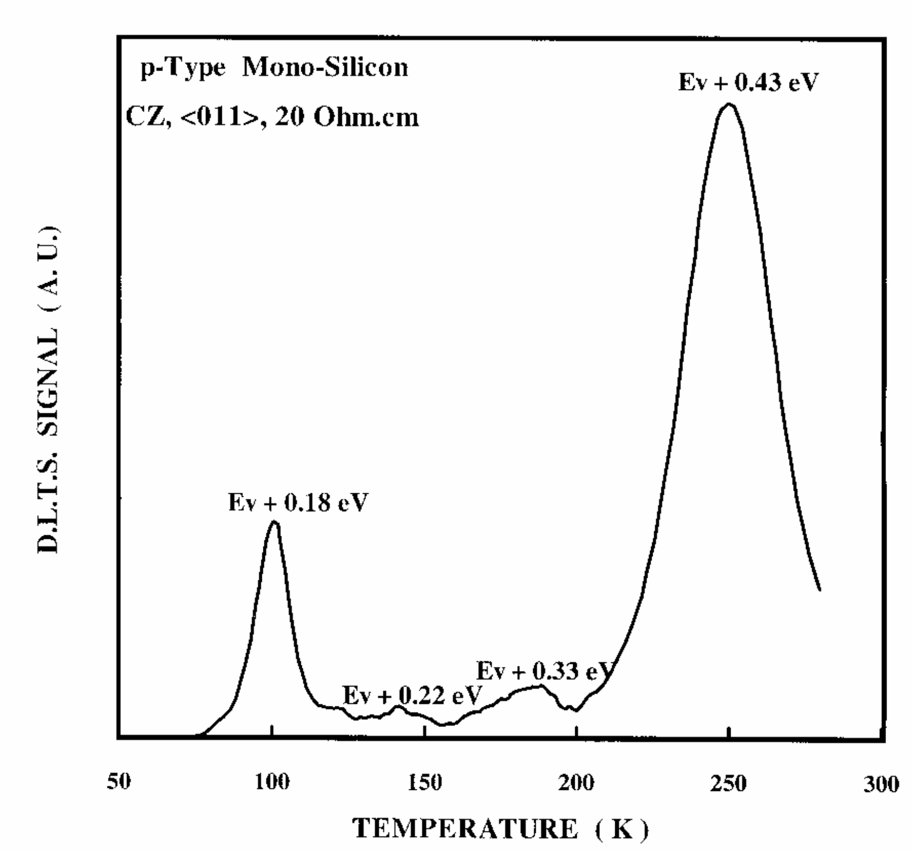

Fig. 7: D.L.T.S. spectrum from Al-Si(P) Schottky diodes after incoherent light thermal processing at 850 °C, for 10 s, under Argon atmosphere, in Rapid Thermal Annealing Furnace.

REFERENCES

[1] R. Singh, J. Appl. Phys., 63, 8 (1988) p. R59.

[2] A. Barhdadi, H. Amzil, R. Stuck, C. Ganter, J-C. Muller and P. Siffert, J. Chim. Phys., 88, 10 (1991) p. 2217.

[3] A. Barhdadi, H. Amzil, N. M'gafad, T. Biaz, W. Eichhammer, J-C. Muller and P. Siffert, Journal of Alloys and Compounds, 188 (1992) p. 221.

[4] A. Barhdadi, H. Amzil, J-C. Muller and P. Siffert, 13th European Photovoltaic Solar Energy Conference and Exhibition, 23 - 27 Oct. 1995, Nice, France.

[5] M. Toulemonde and P. Siffert, Appl. Phys., 25 (1981) p. 139.

[6] W-O. Adekoya, J-C. Muller and P. Siffert, Appl. Phys., A 42 (1987) p. 227.

[7] Y-N. Nikiforov and V-A. Yanushkevich, Sov. Phys. Semicond., 14 (1980) p. 314.

[8] L-C. Kimerling and J-L. Benton, In "Laser and Electron Beam Processing of Material", Ed. by C-W. White and P-S. Peercy (Academic, New-York 1980) p. 385.

[9] A. Mesli, J-C. Muller and P. Siffert, In "Laser-Solid Interactions and Transient Thermal Processing of Materials", Suppl. of J. de Physique., C 44, 5 (1983) p. 281.

[10] A.Slaoui, A.Barhdadi, J-C.Muller and P.Siffert, Appl. Phys., A39 (1986) p. 159.

[11] A. Barhdadi and J-C. Muller ICTP preprint N° IC/98/130.

[12] K. Graph and H. Pieper, J. Electrochem. Soc., 128, 3 (1981) p. 669.

[13] D. Barbier, M. Remram, J-F. Joly and A. Laugier, J. Appl. Phys., 61 (1987) p. 156.

[14] K. Wunstel and P. Wagner, Solid. Stat. Commu., 40 (1981) p. 797.

[15] J-D. GERSON, L-J. CHENG and J-W. CORBETT, J. Appl. Phys., 48, 11 (1977) p. 4821.

[16] W-O. Adekoya, Ph.D. Thesis, University of Paris VII, 1987, France.

[17] P-M. Mooney, L-J. Cheng, M. Suli, J-D. Gerson and J-W. Corbett, Phys. Rev. B, V15, 8 (1977) p. 3838.

[18] E. Sonder and L-C. Templeton, J. Appl. Phys., 36 (1965).

[19] E-M. Lawson and S-J. Pearton, Phys. Stat. Sol., A72 (1982) p. K155.

[20] B. Hartiti, Ph.D. Thesis, University Louis Pasteur I, Strasbourg 1990, France.

[21] K-L. Wang, Y-S. Lin, G-E. Possin, J. Karins and J. Corbett, J. Appl. Phys., 54 (1983) p. 3839.