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CARRIER TRAPS IN GRADED InGaAs PHOTODIODES WITH HIGH INDIUM CONTENT

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Dedicated to Professor Mladen Paić on the occasion of his 90$^{\mathbf{th}}$ birthday

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Carrier traps in $In_{0.82}Ga_{0.18}As$, introduced during manufacturing of photodiodes by vapour phase epitaxy (VPE), have been studied by electrical measurements. Two groups of localized energy levels associated with traps were found in photodiodes annealed at higher temperature after fabrication: the first, at $E_c - 0.14$ eV, and the second located deeper, close to the middle of the energy gap. Electrically activated dislocations by association with some impurities are responsible for the occurrence of the deeper levels.

1. *Introduction*

$In_xGa_{1-x}As$ compounds are of considerable interest as materials for manufacturing of photodiodes that can detect efficiently near-infrared radiation down to about 2.5 μm and operate at room temperature. Most of the published data are dealing with lattice-matched $In_{0.53}Ga_{0.47}As$ alloys, epitaxially grown on InP substrates [1-4], with the cut-off at 1.7 μm, thus covering silica fiber lightwave communication bandwidth from 1.0 to 1.65 μm. However, with the development of low loss metal fluoride glass fibers, operating at 2.5 μm, it became necessary to develop materials and fast photodiodes with responsivity beyond the standard cut-off at 1.7 μm. This can be done by increasing the indium content in $In_xGa_{1-x}As$ compounds. For instance, a suitable alloy is $In_{0.88}Ga_{0.12}As$ with the energy gap of 0.45 eV, thus responding up to 2.6 μm. However, due to a serious mismatch in lattice parameters between this alloy and the InP substrate, amounting to more than 2 percent, the so-called graded layer technique should be employed [5] in order to prevent propagation of misfit dislocations from the substrate into the active InGaAs absorption layer. It is necessary to change the composition of ternary alloys in discrete steps during the epitaxial growth starting with the lattice matching alloy. The abrupt steps in composition tend to turn upward propagating inclined misfit dislocations into the growth plane, thus preventing their entry into the active regions of the device.

In general, InGaAs photodiodes have been grown by liquid phase epitaxy (LPE) [2], metal organic chemical vapour deposition (MOCVD) [3], and by vapour phase epitaxy (VPE) [4,5] in mesa or planar configuration. One of the main technological problems in obtaining low noise photodiodes is to reduce surface leakage currents. Dark currents of less than 1 nA are often required for fiber communication systems and imaging applications using discrete devices or pixel arrays. This may be accomplished by growing a cap or window layer on top of the InGaAs absorption layer, and by passivating the photodiode by SiO_2 or SiN_x anti–reflection (AR) coating. In these technological processes, it is necessary to reduce as much as possible the introduction of various electrically active defects acting as traps or carrier generation centers. In a narrow–gap photodiode of planar configuration, with numerous heterostructure interfaces, this is a very difficult task.

The purpose of this paper is to present results of some electrical measurements on encapsulated photodiodes with the $In_{0.82}Ga_{0.18}As$ absorption layer and with the lattice-matched $InAs_{0.6}P_{0.4}$ cap layer in order to find out the concentration of various defects, their properties and locations in the structure of the photodiodes prepared under different conditions and even annealed after fabrication. This may lead to a better understanding of the significance and efficiency of some specific technological steps in numerous attempts to reduce the diode dark current, thus improving the diode properties.

2. *Experimental*

Photodiodes were formed by Zn diffusion into the absorption layer through a 75 μm opening in the SiN passivation layer. The first subabsorption layer had the same composition as the cap layer. The graded substrates were composed of 17 to 19 $InAs_yP_{1-y}$ layers with y decreasing from 0.6 to 0.0. All epitaxial layers were grown by hydride VPE on sulphur-doped n-type InP (as shown in Fig. 1).

In contrast to the standard procedure of growing the absorption InGaAs layer with an effective donor concentration of the order of 10^{16} cm^{-3}, the absorption n-type layer was intentionally sulphur-doped to about 5×10^{16} cm^{-3}.

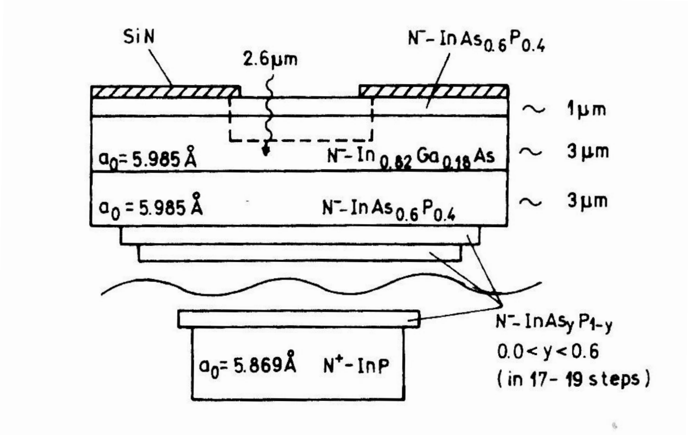

Fig. 1. Compositionally graded $In_{0.82}Ga_{0.18}As/InAs_{0.6}P_{0.4}$ *detector structure for the 2.6* μm *response.*

Measurements were made with three groups of photodiodes. The first group was annealed ten times for less then an hour in the temperature range from 400 to 640 °C, after stripping the SiN passivation layer (designated as 09AS, 10AS and 06AS). Photodiodes of the second group were also thermally treated ten times but with the SiN layer (85NS, 86NS and 87NS samples). The third group was not annealed after fabrication (17NA, 18NA and 19NA samples).

Deep level transient spectroscopy (DLTS) measurements were performed by Sula Technology Deep Level Spectrometer and IOtech, Inc. ADC 488/8S analog-to-digital converter, enabling simultaneous recording and storage of four DLTS spectra with different "rate windows" in a single temperature scan.

Current-voltage ($I-V$) characteristics in the dark as a function of temperature were done in a BioRad cryostat using a Keithley Model 617 Programmable Electrometer. Capacitance-voltage ($C-V$) characteristics were taken by a Boonton 75C Bridge.

3. *Results and discussion*

a) $C-V$ measurements

$C-V$ curves taken at room temperature at the signal frequency of 500 kHz are shown in Fig. 2. The data deviate slightly from the $V^{-1/2}$ dependence. From the slopes of the curves at small reverse bias, it is possible to calculate the effective concentration of donors in the n-type In-Ga-As absorber material (see Table 1).

In spite of intentional doping, much lower donor concentrations were obtained that indicate that some acceptors were also introduced, compensating electrical activity of the donors and shifting the Fermi level close to the middle of the forbidden energy gap.

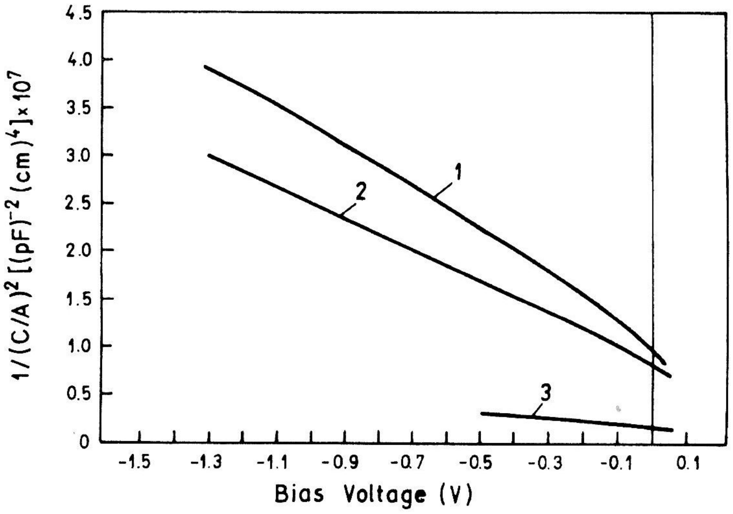

Fig. 2. $C - V$ curves of different photodiodes determined at 500 kHz*: 1–87NS, 2–09AS, 3–18NA.*

TABLE 1.
Active areas of differently treated photodiodes and their effective donor concentrations.

Photodiode	Active photodiode area (cm^2)	$N_D - N_A$ (cm^{-3})
17NA	2.28×10^{-3}	3.3×10^{14}
18NA	2.00×10^{-3}	4.1×10^{14}
09AS	4.28×10^{-3}	6.9×10^{13}
10AS	4.06×10^{-3}	7.7×10^{13}
06AS	3.52×10^{-3}	9.7×10^{13}
86NS	2.66×10^{-3}	1.2×10^{14}
87NS	4.28×10^{-3}	4.4×10^{13}

b) $I - V$ measurements

Forward $I - V$ characteristics at different temperatures of annealed and SiN stripped photodiodes (AS samples) show the value of the ideality factor n close to 1 for temperatures higher than 280 K, indicating that the diffusion mechanism dominates the forward current at higher temperature. At lower temperature, recombination components start to contribute increasingly more to the forward current and the ideality factor of the 06AS photodiode is equal to 1.11, 1.39 and 1.79 at 260, 230 and 200 K, respectively. Similar temperature dependence was observed for photodiodes from other groups.

The extrapolated intercepts $I(0)$ on the current axis of the linear portion of the forward $I-V$ curves follow $I(0) \sim \exp(-\Delta E/kT)$ dependence with ΔE around 0.48 eV at higher temperatures, close to the band gap energy, and equal to 0.23 and 0.28 eV at lower temperature for the 06AS and 10AS photodiodes, respectively.

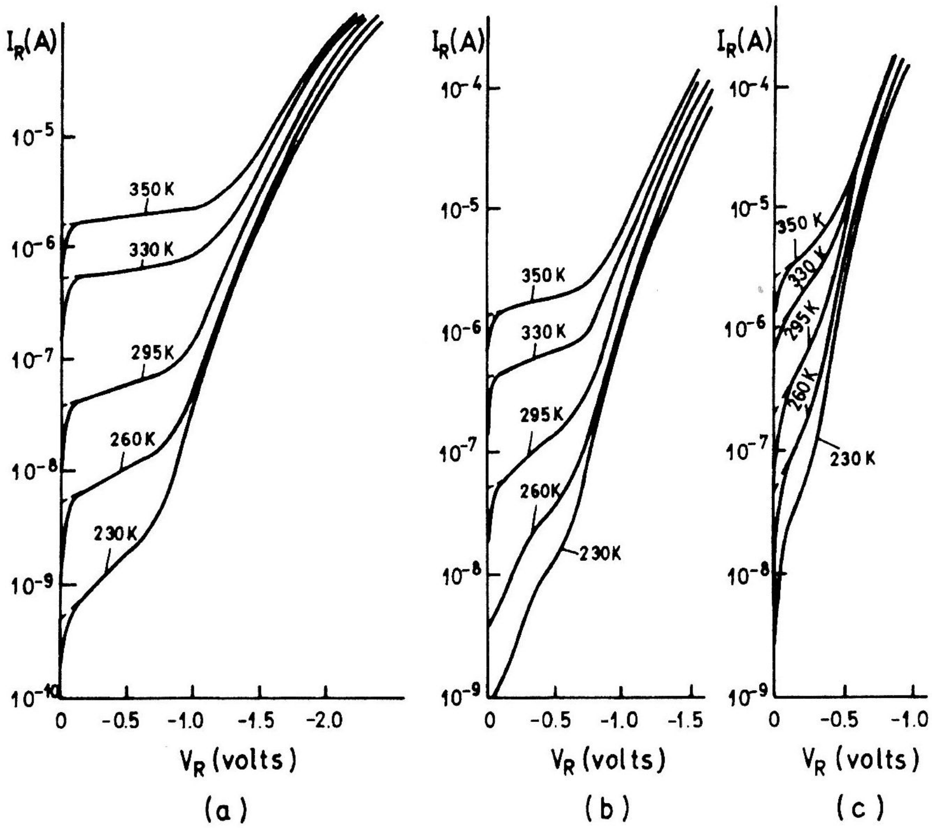

Fig. 3. Temperature dependence of the reverse $I-V$ characteristics of: (a) 87NS, (b) 06AS and (c) 18NA photodiodes.

Reverse current-voltage characteristics are shown in Figs. 3a, b and c. For the 87NS photodiode, at $V = -100$ mV, the lowest current was equal to 40.9 nA at room temperature decreasing to 0.65 nA and 26 pA (6.1×10^{-9} A/cm^2) at 230 and 200 K, respectively.

The Arrhenius plots ("cooling slopes"), $\log I_R$ vs. $1/T$ curves of different photodiodes, taken at the middle of the "plateau", i.e. at – 0.3, – 0.4 and – 0.5 V for NA, AS and NS groups, respectively, were performed, too. At higher temperatures, the slopes approach the energy gap value of 0.48 eV for all photodiodes. At lower temperatures, the non-annealed samples exhibit leveling-off, indicating freeze-out of carriers from a very shallow sulphur donor level. More compensated 06AS and

87NS samples in this temperature range show energy levels with ionization energies of 0.14 and 0.16 eV, respectively.

All the diodes are characterized by small breakdown voltages with the band-to-band tunneling mechanism dominating the dark current for reverse bias voltages greater than 0.5, 0.8 and 1.2 V for NA, AS and NS groups of diodes, respectively.

c) DLTS measurements

It was somewhat surprising that none of the non-annealed graded photodiodes showed a DLTS peak in the whole accessible range of frequencies and temperatures. One can not conclude that there are no impurity levels in these samples, as the DLTS method is insensitive to the energy levels located closer than about 0.05 eV from the energy band edges. Such an energy level is associated with the sulphur donor and located at less than 0.01 eV below the conduction band edge.

The annealed and SiN non-stripped samples (NS) are characterized by a DLTS peak occurring at low temperatures (around 100 K) in a low concentration equal to 2.5×10^{11} cm^{-3}, as determined from the relation

$$N_T = 2N_D^* \frac{\Delta C}{C}, \tag{1}$$

where N_D^* is the effective donor concentration taken to be equal to 1×10^{14} cm^{-3}.

The apparent energy level E_t is located at (0.14 ± 0.02) eV below the conduction band, as obtained from the Arrhenius plot ($\ln(\tau T_m^2)$ vs. T_m^{-1}) under the assumption that the temperature dependence of the entropy is negligible, and disregarding the temperature dependence of the capture mechanism.

Under the same assumptions, and taking the level degeneracy factor $g = 1$, the electron capture cross–section σ_n of this trap, calculated from the relation [6]

$$\frac{1}{\tau_n} = e_n = g^{-1} \sigma_n \sqrt{\frac{8k}{\pi} m_n^*} \sqrt{T_m} N_c T_m^{3/2} \exp(-E_d/kT_m), \tag{2}$$

exhibits an extremely large value of 9×10^{-12} cm^2. τ_n is the time constant (rate window), e_n the electron emission rate, k the Boltzmann constant, T_m temperature of the DLTS peak, and N_c the density of states in the conduction band. The effective electron mass, m_n^*, has been taken to be equal to 0.035 m_0, the value obtained by interpolation of the effective electron mass of 0.03 m_0 for InAs and 0.069 m_0 for GaAs [7]. Such a huge electron capture cross–section would suggest that the trap is positively charged, attracting electrons by Coulomb interaction. In our DLTS set-up, where the rate window τ is related to the initial delay by the simple relation $\tau = 4.3\times$ initial delay, this trap has been detected only for the initial delays shorter than 0.2 ms, as for longer initial delays the DLTS peaks would occur at temperatures below 80 K.

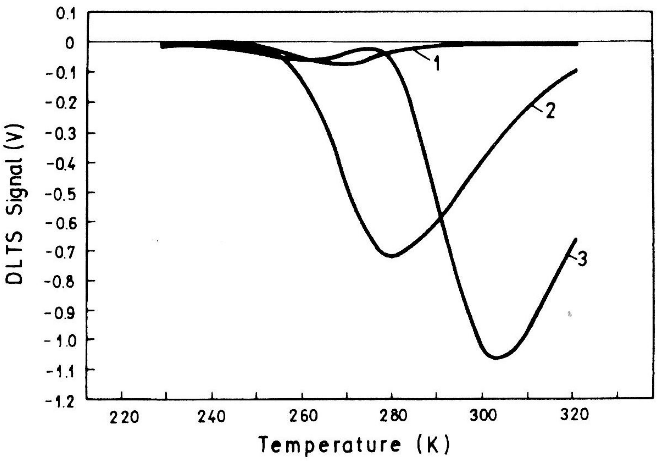

Fig. 4. DLTS spectra of the 09AS photodiode taken with pulse length of 5.5 ms, *period of* 20 ms, *at the reverse bias of* 0.8 V, *and delay times of:* $1-0.2$ ms, $2-0.05$ ms *and* $3-0.02$ ms.

The annealed samples with silicon nitride stripped and reapplied (AS) show DLTS signals of very large magnitude after they were kept in darkness for several days, for holding at temperatures higher than 320 K for some time, and biasing the sample to reverse voltage at the beginning of the breakdown region. The curves are shown in Fig. 4. However, in the subsequent measurements, the magnitude of the peaks have decreased by an order of magnitude, corresponding to the concentration of traps of 2.8×10^{12} cm^{-3}, as calculated from Eq. (1). The DLTS peaks are observable only for initial delays shorter than 0.2 ms, increasing in magnitude for shorter rate windows, and only for pulses longer than 5.5 ms. They correspond to electron traps in the n-type absorber of the photodiode located at 0.24 eV below the conduction band and with the electron capture cross–section of 2.7×10^{-15} cm^2, calculated under the same assumptions as stated earlier. These DLTS peaks, remeasured at a later time, shift to higher temperatures with the corresponding energy level at 0.28 eV, the electron capture cross–section of 3.9×10^{-15} cm^2, and with an increase in the trap concentration up to 4.3×10^{12} cm^{-3}.

Double correlation deep level spectroscopy (DDLTS) measurements were done in order to check whether these traps are associated with surface effects. DDLTS data have proved that the traps are located in the bulk, close to the p-n junction, exhibiting the same energy level at $E_c - 0.28$ eV.

4. Conclusions

Based on the results presented in the preceding paragraphs, the following conclusions can be made:

1. In the process of deliberate doping of n-type InGaAs with sulphur dopants,

compensating (native?) acceptors are introduced simultaneously, thus reducing the effective donor concentration and increasing resistance of the active absorption layer.

2. The non-annealed samples have the largest reverse dark currents, the largest effective donor concentration, the largest contribution of the generation-recombination component in the current conduction, and the smallest breakdown voltage. The absence of DLTS-visible defects indicates that the gradual lattice-matching procedure was efficient in preventing propagation of electrically active dislocations from the substrate into the active part of photodiodes.

3. The process of annealing after fabrication of photodiodes reduces further the leakage current but introduces or activates electrically complex defects in the bulk or at the interfaces. The $E_c - 0.14$ eV level, corresponding to the trap with a large carrier capture cross–section, is similar to the one observed in low pressure MOCVD grown InGaAs alloy with high indium content [8]. It has also been detected in the lattice-matched InGaAs/InP systems [3]. As there is no such level in non-annealed samples, it is unlikely that its origin is connected with the zinc diffusion, in accordance with the previous findings [8]. It seems that it is localized in the InGaAs layer close to the cap-absorption layer interface.

4. SiN stripping and reapplication prevents the appearance of the shallower trap characterised by the DLTS peak around 100 K, and introduces a deep trap in the lower half of the energy gap, from 0.24 to 0.28 eV below the conduction band, i.e., close to the middle of the gap that is normally occupied by electrons as it is located below the Fermi level. The same trapping levels were observed previously in the case of 2.6 μm cut-off photodiodes, VPE grown by the standard procedure [9].

5. Long trap filling pulses, required to reveal the deep trap in the DLTS spectra, indicate that the defect exists in a charged state after the emission process like a double donor, and the Coulomb wells around these centres are lowered by high electric fields in the depletion region, enhancing the emission rate. Therefore, the ionization energies determined by DLTS may have been too small and should be corrected for the Poole-Frenkel effect. Corrections should be also necessary to account for the nonexponential behaviour of transients. The shape of DLTS signals and their pulse length dependence would suggest that dislocations are associated with the occurrence of the trap energy distribution. They may be electrically activated during the annealing treatment by association with some diffusing impurity.

6. Irregular changes and instabilities in the capacitance of the photodiodes, sometimes observed at the beginning of DLTS measurements during the initial cooling down and heating up sequence, may be associated with some mobile charges in the passivating layers or at the interfaces.

7. A very peculiar behaviour of deep traps in the annealed InGaAs photodiodes merits some further careful investigation, especially concerning the capture mechanism and its temperature dependence.

References

1) S. R. Forrest, I. Camlibel, O. K. Kim, H. J. Stocker and J. R. Zuber, IEEE Trans. Electron. Devices Lett. **EDL-2** (1981) 283;
2) O. K. Kim, B. V. Dutt, R. J. McCoy and J. R. Zuber, IEEE J. Quantum Electron. QE-21 (1985) 138;
3) P. Philippe, P. Poulain, K. Kazmierski and B. de Cremoux, J. Appl. Phys. **59** (1986) 1771;
4) S. R. Forrest, V. S. Ban, G. Gasparian, D. Gay and G. H. Olsen, IEEE Trans. Electron. Devices Lett. **9** (1988) 217;
5) R. U. Martinelli, T. J. Zamerowski and P. A. Longeway, Appl. Phys. Lett. **53** (1988) 989;
6) Landolt-Börnstein, *Numerical Data and Functional Relationship in Science and Technology*, Volume **22**, *Semiconductors*, Subvolume b, ed. by M. Shulz, Springer-Verlag, Berlin, 1989;
7) H. F. Wolf, *Semiconductors* (Wiley-Interscience, New York, 1971) p. 30;
8) D. Pogany, F. Ducroquet, S. Ababou and G. Bremond, J. Electrochem. Soc. **140** (1993) 560;
9) V. S. Ban, A. M. Joshi and N. B. Urli, in Proc. International Symposium on Physical Concepts and Materials for Novel Optoelectronic Device Applications II, Trieste, 24-28 May 1993, Paper No. 198538.

ZAMKE ZA NOSITELJE NABOJA U STUPNJEVANIM InGaAS FOTODIODAMA S VELIKIM SADRŽAJEM INDIJA

Električnim mjerenjima istražena su svojstva zamki za nositelje naboja koje nastaju pri izradi fotodioda iz $In_{0.82}Ga_{0.18}As$ metodom epitaksijalnog rasta iz parne faze (VPE). U fotodiodama, koje su naknadno napuštane nakon izrade na povišenoj temperaturi, zapažene su dvije skupine lokaliziranih nivoa zamki: jedan plići na $E_c - 0,14$ eV i druge dublje nešto ispod sredine zabranjenog energijskog pojasa. Ustanovljeno je da su električki aktivirane dislokacije primjesama odgovorne za pojavu dubljih nivoa.