Highlights

N GaAs

Microwave induced transformation of defect in SiC and
Oleg Olikh, Petro Lytvyn
The microwave irradiation increase interstitial defect concentration at near surface region
• Stress intensity the microwave induced defect transformation
• Microwave treatment decreases σ_n of vacancy related defects in SiC and GaAs monocrystal
• The transient acoustoelectric spectroscopy used for determining properties of defects in SiC and GaAs.
• A microwave annealing of defects in SiC and GaAs was observed.

Microwave induced transformation of defect in SiC and GaAs

Oleg Olikh^{a,*}, Petro Lytvyn^b

^aPhysics Faculty, Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Street, Kyiv, 01601, Ukraine
^bV. Lashkaryov Institute of Semiconductor Physic of NAS of Ukraine, 41, pr. Nauki, Kyiv, 03028, Ukraine

Abstract

The influence of microwave radiation (2,45 GHz, 1,5 W/cm², up to 80 s) on defects was studied in monocrystals n-6H–SiC, n-GaAs and epi-GaAs. The capture cross-section of charge carrier have been found to change and defect complexes to be reconstructed due to the growing number of interstitial atoms in the near surface layer. The correlation between the changes in defect sub-system and deformation of the near surface layer is analyzed. The possible mechanisms of the revealed effects are discussed.

Keywords: Microwave, SiC, GaAs, Defect transformation

1. Introduction

Microelectronics is a field of primary importance today, and the investigation of how semiconductors and their structure properties change under the action of various external factors has become one of the most important tasks in material science. A great number of theoretical and experimental researches have been aimed at revealing degradation mechanisms in microelectronic devices and finding new technologies of their production. The influence of certain factors, for example, radiation, has been studied quite well --- see, for instance, Kozlovskii et al. (2000); Schrimpf and Fleetwood (2004). At the same time, new agents begin to attract more attention, such as ultrasound loading (USL) (Olikh et al. (2018); Olikh and Pinchuk (2006)), or microwave treatment (MWT)(Kitchen et al. (2014); Zohm et al. (2000); Bhunia and Bose (1998); Bacherikov et al. (2003); Pashkov et al. (1994); Boltovets et al. (2002); Milenin et al. (1994); Belyaev et al. (2002); Ashkinadze et al. (1996); Ermolovich et al. (1998); Belyayev et al. (1998); Bacherikov et al. (2008); Zayats et al. (2015); Belyayev et al. (2012)). As for the latter, superhigh frequency (SHF) electromagnetic radiation has found wide application due to its capability to heat solid bodies (Kitchen et al. (2014); Zohm et al. (2000)). This approach is peculiar because of its high efficiency, capability to increase temperature homogeneously as well as at chosen locations, and extremely high heating speeds

influence also causes the change in various characteristics of semiconductor materials and device structures. For instance, it has been found that irradiation by SHF causes the relaxation of internal stresses and modification of near surface regions in GaAs and InP structures (Boltovets et al. (2002); Pashkov et al. (1994); Milenin et al. (1994); Belyaev et al. (2002); Ermolovich et al. (1998); Zayats et al. (2015); Belyayev et al. (2012)), the leveling of surface microrelief in SiC/SiO2 structures (Bacherikov et al. (2003)), redistribution of impurities (Bacherikov et al. (2003); Belyayev et al. (1998); Zayats et al. (2015)) and change in charge state in the complexes (Milenin et al. (1994)) as well as generation of defects (Belyayev et al. (1998)). One of the consequences these processes of structure-admixture ordering is the decrease in the range of Schottky diode parameter spread (Milenin et al. (1994), Belyayev et al. (1998)). Moreover, MWT has been found to induce changes in the properties of Ti, Gd and Er films deposited on silicon carbide (Bacherikov et al. (2008)), as well as reconstruction of GaAs photoluminescence spectra (Belyaev et al. (2002); Ermolovich et al. (1998); Belyayev et al. (1998)), the peculiarities of the effect being dependent both on the type of dopant and crystal structure orientation of the samples. As a whole,

these facts allow us to consider MWT as one of the most promising ways of modifying semiconductor devices.

(Kitchen et al. (2014)). As a result, MWT is widely used to synthesize various compounds, semiconduct-

ing compounds including (Kitchen et al. (2014); Bhu-

nia and Bose (1998)). However, this kind of external

Email address: olegolikh@knu.ua (Oleg Olikh)

^{*}Corresponding author

At the same time, the more detailed information about how MWT influences deep center parameters is practically unknown. The aim of our work is to investigate MWT impact on the parameters of deep centers located in the near surface region of n–6H–SiC and n–GaAs single crystals, as well as on GaAs epitaxial structures by means of acoustoelectric transient spectroscopy.

2. Experimental details

It has been reported (Boltovets et al. (2002); Milenin et al. (1994); Belyaev et al. (2002); Ashkinadze et al. (1996); Ermolovich et al. (1998)) that generally, the MWT impact on semiconductor structures depends on many factors. The main of them are the initial level of structural perfectness, conductivity, dielectric permittivity and structure topology. In order to estimate how MWT affects the defect parameters we chose different samples in view of doping degree, initial level of residual mechanical stress as well as structure. They were as follows

- i) Single crystal n–6H–SiC wafers, grown by Leli method and doped with nitrogen. The samples were: 490 μ m thick plates with dimensions $5 \times 10 \text{ mm}^2$ and carrier concentration $(3-6)\times10^{18}$ cm⁻³ (further on SIC1 and SIC2); and 460 μ m thick wafer of the same dimensions with concentration of carriers $(1-3)\times10^{18}$ cm⁻³ (SIC3).
- ii) GaAs single crystal plates with thickness of 300 μ m. The plates were (100) oriented, doped with tin, the concentration of electrons was $(1.5-2.5)\times 10^{18}~{\rm cm}^{-3}$ for sample GAS1 and $(3-5)\times 10^{16}~{\rm cm}^{-3}$ for sample GAS2. GAT denotation is used for wafer (111), which was doped by tellurium, $n=(1-2)\times 10^{18}~{\rm cm}^{-3}$.
- iii) Epitaxial n-n⁺ structures of GaAs which were $300 \, \mu \mathrm{m}$ thick single crystal substrates $n = 2 \times 10^{18} \, \mathrm{cm}^{-3}$ covered with 6 $\mu \mathrm{m}$ thick layer with carrier concentration $3.9 \times 10^{15} \, \mathrm{cm}^{-3}$ (sample GAE1), $3.5 \times 10^{15} \, \mathrm{cm}^{-3}$ (GAE2), $5.0 \times 10^{15} \, \mathrm{cm}^{-3}$ (GAE3). The substrate and epitaxial layer were doped with tellurium.
- iv) Epitaxial n-n⁺-n⁺⁺ structures of GaAs:Te with a buffer layer. They were made from single crystal (100) substrate (300 μ m, $n = 2 \times 10^{18}$ cm⁻³) subsequently covered with 1 μ m layer with $n = 8 \times 10^{16}$ cm⁻³ and 2 μ m layer with $n = 7 \times 10^{15}$ cm⁻³. Two samples (GAB1 and GAB) were cut from different wafers and used in the investigation.

Epitaxial systems produced by the gas phase epitaxy technique. The samples used in the experiment are categorized in Fig. 1.

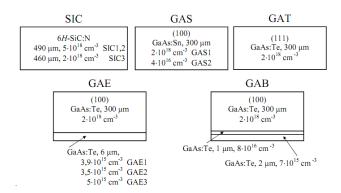


Figure 1: Sample structures for deep level investigations

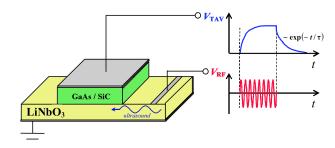


Figure 2: Scheme of TAV signal measurements. Time dependence of radio impulse $V_{\rm RF}$ of ultrasound excitation in piezoelectric plate and the resulting TAV signal $V_{\rm TAV}$ are shown schematically

MWT of the sample was carried out in free space at room temperature in the magnetron at the frequency of 2.45 GHz and specific power 1.5 W/cm². The epitaxial structures were irradiated from the side of the epitaxial layer. The total exposition time t_{MWT} varied in the range 20 - 80 s for different samples. To avoid essential heating, the maximum single irradiation exposure time was no more than five seconds.

The parameters of deep centers, such as the efficient cross section of electron capture σ_n and location of the center energy level with relation to conductivity band bottom E_c-Et were determined before and after MWT. For this purpose we used acoustoelectric transient spectroscopy (Ostrovskii et al. (1998); Ostrovskii and Olikh (1998); Gromashevskii et al. (2013); Abbate et al. (1995)). The method is schematically presented in Fig. 2. The samples were placed on the LiNbO3 piezoelectric plate in which acoustic waves were excited as impulses. After ultrasound impulse termination, the relaxation of transverse acoustoelectric voltage (TAV) takes place according to the law

$$V_{\text{TAV}}(t) = V_{\text{TAV},0} \exp(-t/\tau). \tag{1}$$

The simple exponential dependence according to Eq. (1) is observed in cases when only one type of deep

centers is effective in acoustoelectric interactions. For *n*-type semiconductor, the characteristic time of relaxation is described by equation (Ostrovskii et al. (1998); Abbate et al. (1995))

$$\tau = \frac{1}{\sigma_n \, \nu_{\text{th,}n} \, N_c} \exp\left(\frac{E_c - E_t}{kT}\right),\tag{2}$$

where $v_{th,n}$ is the electron thermal velocity N_C is the densities of states in the conduction band.

The experimental measurements of the TAV relaxation at different temperatures and further approximation of the results according to Eq. (1) allowed us to obtain $\tau(T)$ dependence. The E_c-Et was determined from the slop of τ dependence on $(kT)^{-1}$ in semi-logarithmic scale and then, by using Eq. (22), σ_n was calculated. The measurements were performed in the temperature range (290 – 350) K except GAB samples, the TAV for which was high enough to be measured only after heating to above 310 K.

For single crystal samples, before and after MWT, we also determined curvature radius $R_{\rm cur}$ and deformation $\xi_{\rm cur}$ of near surface crystallographic planes. The value of $\xi_{\rm cur}$ was estimated by X-ray method from the change in the angle of diffraction maximum location during sample translation (Godwod et al. (1976)), the curvature was measured by a profilometer DekTak 3030 Veeco Instruments. $R_{\rm cur}$ and $\xi_{\rm cur}$ were measured with a relative error no more than 2 %. For GaAs single crystals, we also analysed the distribution of structural defects over the area using the method of Borman X-ray projection topography, and estimated the distribution of dislocation densities and micro stresses from the analysis of the intensities of Friedel reflection pairs hkl and $hk\bar{l}$.

3. Results and discussion

Fig. 3 presents typical temperature dependences of τ for the samples before and after MWT. The above data show both the curves' slop (which is directly related to the level location in the gap) and the absolute value of characteristic time of relaxation TAV change that after MWT. The character of the impact and how strong it is, depend both on the exposition time and doping as well as internal structure of the samples under study. The obtained results are generalized in Table 1. It is seen that in silicon carbide samples there are two deep levels, labeled ESC1 and ESC2, while in gallium arsenide, they are six (EGA1–EGA6).

The presented data show a number of characteristic features:

- i) The value of the carrier capture cross-section is much more sensitive to MWT than the energy location of the levels. For example, σ_n was found to change by an order of magnitude while the level location displacement was no more than 20%; moreover, capture cross-section was found to modify at lower exposition times: for instance, the value of $(E_c E_t)$ for GAB1 practically did not change after 20 s MW exposition, while σ_n grew about four times.
- ii) In single crystals, the MWT induced changes become stronger as the free charge carrier concentration decreases (see data on samples GAS1 and GAS2) and the relative deformation increase (the increase of surface curvature).
- iii) After durable MWT of single crystal samples ($t_{\rm MWT} > 40$ s for GaAs, $t_{\rm MWT} > 80$ s for SiC), TAV signal essentially decreases. This fact correlates with data from (Belyayev et al. (1998)), where it is reported about the decreased concentration of the centers with levels in the upper half of the band gap in the result of MW annealing.
- iv) The irradiation dose required to change essentially the parameters of the centers in epitaxial structures is higher than that for single crystal samples. In particular, Table 1 provides data for the samples of GA and GAB series after 20 s MWT that support this fact. It should be noted that the doping level of GAB and GAE substrates was the same as that of samples GAS1 and GAT, the doping level of GAB epitaxial layer was similar to GAS2. In addition, GAB, GAE and GAT contained the same doping impurity. Thus, the found differences are determined by the structure of the samples, but not by the difference of their conductivities.
- v) The character of changes in single crystal wafers and epitaxial structures is opposite: σ_n and $(E_c E_t)$ have been found to decrease after MWT of SIC, GAS, GAT, while for GAE and GAB both parameters increase.

We shall now consider the possible configuration of the centers discovered in the structures under study. For this purpose we should take into account that the reported data for the trap main parameters vary in a wide range, in particular the difference between the values of capture cross-sections can be as big as four orders of magnitude (Pavlović et al. (2000)). One of the possible reasons of such a big spread can be an essential dependence of thermal charge emission speed on the electric field strength (Bulyarskii et al. (2000); Makram-Ebeid and Lannoo (1982)) caused by a) decrease of ionization energy due to Pool–Frenkel effect or, for example, Coulombic interactions of centers (Stellmacher et al. (2001)); b) change of σ_n value (Bourgoin and De Angelis (2001)). As a rule, the change in $(E_c - E_t)$ comprises

Table 1: The determined defect parameters in samples n-GaAs and n-6H-SiC

Sample	t_{MWT} , s	Level	$(E_c - E_t)$, eV	σ_n , cm ^{2 a)}	R _{cur} , m	ξcur
SIC1	0	ESC1	0.33 ± 0.01	$(7 \pm 4) \cdot 10^{-18}$	∞ ∞	0
	20	ESC1	0.33 ± 0.01	$(5 \pm 3) \cdot 10^{-19}$	170.2	$8.7 \cdot 10^{-7}$
	40	ESC2	0.26 ± 0.01	$(2 \pm 1) \cdot 10^{-19}$		
	80		weak sigi			-
SIC2	0	ESC1	0.33 ± 0.01	$(7 \pm 4) \cdot 10^{-18}$	> 2000	$< 1.2 \cdot 10^{-7}$
	20	ESC1	0.33 ± 0.01	$(5 \pm 3) \cdot 10^{-19}$	171.9	$1.4 \cdot 10^{-6}$
SIC3	0	ESC1	0.34 ± 0.02	$(3 \pm 2) \cdot 10^{-18}$	3.8	$6.1 \cdot 10^{-5}$
	20	ESC2	0.29 ± 0.01	$(5 \pm 3) \cdot 10^{-19}$	5.5	$4.2 \cdot 10^{-5}$
	40	ESC2	0.26 ± 0.01	$(10 \pm 7) \cdot 10^{-20}$		
	80	ESC2	0.23 ± 0.01	$(6 \pm 4) \cdot 10^{-20}$		-
GAS1	0	EGA1	0.32 ± 0.02	$(3 \pm 2) \cdot 10^{-17}$	-53.8	$-2.8 \cdot 10^{-6}$
	20	EGA1	0.31 ± 0.01	$(2 \pm 1) \cdot 10^{-17}$	22.9	$6.5 \cdot 10^{-6}$
	40		weak sign			-
GAS2	0	EGA1	0.32 ± 0.01	$(4 \pm 2) \cdot 10^{-17}$	17.2	$8.7 \cdot 10^{-6}$
	20	EGA2	0.28 ± 0.01	$(5 \pm 2) \cdot 10^{-18}$	14.7	$1.0 \cdot 10^{-5}$
	40		weak sign			
GAT	0	EGA3	0.49 ± 0.02	$(5 \pm 3) \cdot 10^{-14}$		
	20	EGA4	0.40 ± 0.02	$(2 \pm 1) \cdot 10^{-15}$		
GAE1	0	EGA5	0.24 ± 0.01	$(2 \pm 1) \cdot 10^{-18}$		
	60	EGA2	0.29 ± 0.01	$(10 \pm 6) \cdot 10^{-18}$		
GAE2	0	EGA5	0.25 ± 0.01	$(2 \pm 1) \cdot 10^{-18}$		
	60	EGA2	0.30 ± 0.01	$(2 \pm 1) \cdot 10^{-17}$		
GAE3	0	EGA6	0.43 ± 0.01	$(8 \pm 5) \cdot 10^{-17}$		-
	60	EGA6	0.46 ± 0.02	$(7 \pm 4) \cdot 10^{-16}$		
GAB1	0	EGA4	0.39 ± 0.01	$(10 \pm 7) \cdot 10^{-18}$		
	20	EGA4	0.39 ± 0.01	$(4 \pm 2) \cdot 10^{-17}$		
	40	EGA6	0.43 ± 0.02	$(10 \pm 6) \cdot 10^{-17}$		
GAB2	0	EGA4	0.40 ± 0.01	$(10 \pm 6) \cdot 10^{-17}$		
	20	EGA4	0.41 ± 0.01	$(10 \pm 6) \cdot 10^{-17}$		
a) –	40	EGA6	0.45 ± 0.02	$(4 \pm 2) \cdot 10^{-16}$		
a at $T =$						

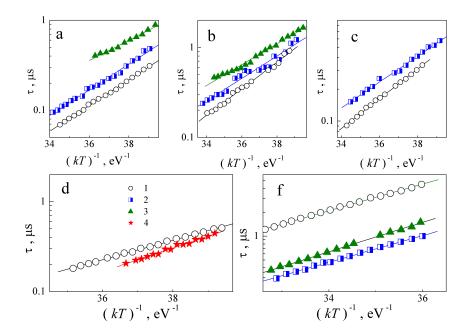


Figure 3: Dependences of TAV relaxation time on inverse temperature for samples SIC2 (a), SIC3 (b), GAS2 (c), GAE2 (d) and GAB1 (e) before and after MWT. t_{MWT}, c: 0 (curves 1), 20 (2), 40 (3), 60 (4)

several hundredth of eV and change of capture crosssection reaches several orders of magnitude: for instance, according to (Bourgoin and De Angelis (2001)), at room temperature, σ_n for EL2 center in GaAs at intensity of 10⁵ V/cm decreases 200 times. As a result, the different methods used for investigating defects yield essentially different parameters for the same centers. As an example, we can compare, from the reviews on various traps in gallium arsenide, the data obtained by methods of deep level transient spectroscopy (Bourgoin et al. (1988)) and thermally stimulated current (Pavlović et al. (2000)). The data were obtained for the defects with closely located levels and very different values of capture cross-section. Generalising the above said, we should note that it is the energy location of traps that we shall be oriented toward in our research.

The position of ESC1 level ($E_c - (0.33 - 0.34)$ eV) observed in the initial crystals of silicon carbide can be compared with the position of S-center ($E_c - 0.35$ eV) (Lebedev (1999); Anikin et al. (1991a,b)), EK-center ($E_c - 0.34$ eV) (Kuznetsov and Edmond (1997)) or (-/+) level center E1 ($E_c - 0.34$ eV) (Lebedev (1999)). S-center is responsible for non-radiative recombination and in 6H-SiC it is a self-interstitial defect (Lebedev (1999)). According to the results reported in (Anikin et al. (1991a,b)), S-center and R-center ($E_c - 1, 27$ eV) are associated with two different charge states of one and the same defect, while according to (Lebedev et al.

(2000)) R-center is a divacancy $V_{Si}V_C$. A complex of silicon vacancies is associated with level E1, which is the center of negative correlation energy (Lebedev et al. (2001)). After MWT, the position of the level responsible for TAV generation in SiC moves to $E_c - (0.26 - 0.29)$ eV (level ESC2). And this situation is also ambiguous: closely located are donor level (0/+) of center E1 ($E_c - (0.27 - 0.28)$ eV (Hemmingsson et al. (1999))) and center X1 ($E_c - 0.3$ eV (Lebedev et al. (2001))). The authors of the latter publication report about the essential dependence of X1 concentration on the crystal structural perfection. They stress that this center is not identical to center E1.

The data for every of the levels revealed in gallium arsenide are given in Table 2. The presented data show that the centers are associated with intrinsic vacancy-related defects.

There are several factors that cause the trap parameters to change. They are as follows.

- i) Transformation of the defect complex due to decay, involvement of additional components, change in distance between the defect components, etc.
- ii)Change of the defect charge.
- iii) Changes in the trap environment, which can result, for instance, in modified strength of electric field around the defect.
- iv) Change in concentrations of the given type of defects: for instance, it is reported in (Stellmacher et al. (2001)) that the change in ionization energy is proportional to the cubic root of the defect concentration.

The analysis of the observed changes should take into account the probable mechanisms of microwave radiation impact on crystals. In the first place, the effect of temperature increase should be analyzed. It is believed that structural modification in the result of MWT is mostly caused by the change in defect charge state and elastic stress fields arising in instantly heated defect regions. However, these processes are known to become intensive at the increased free charge carrier concentrations (Kitchen et al. (2014)), while in our case the effects weaken with the n growth (samples GAS1 and GAS2). Moreover, the applied mode of irradiation did not imply long term continuous exposure to MW oscillations, which reduced the heating of structure as a whole. On the other hand, numerous researches show that the observed effects of MWT cannot be explained only by the mechanisms of fast thermal annealing, so athermal factors should be considered as well. In the recent research, more attention has been paid to nonthermal mechanisms of MWT action (see, for example (Nozariasbmarz et al. (2018)) and the references it contains) which cause dislocation generations and result in smaller clusters of point defects in semiconductor wafers (Ermolovich et al. (2007)), or even trigger recrystallization processes (Nozariasbmarz et al. (2018)). The possible non-thermal processes causing changes in structural characteristics of binary semiconductors were reported in (Ermolovich et al. (2007)). In particular, the processes of dislocation oscillations under the action of electric field were analyzed, and the decorating impurities have been found to influence essentially the behavior of dislocation segments. On the one hand, the available impurities decrease the resonance frequency of oscillations and provide the presence of electric charge, on the other hand, at high oscillation amplitudes they can escape the dislocation, which causes new chemical defects to arise. In their turn, the point defects can perform superhigh frequency oscillations and diffuse in the result of MWT.

The found modifications of deep levels parameters are the result of the above mentioned structural reconstruction in semiconductor near surface regions due to MWT. The results of X-ray investigations show that MWT increases the convexity of single crystal samples, which indicates the aggregation of interstitial defects in the near-surface layer, in particular as a result of the generation of separate dislocations (Boltovets et al. (2002); Belyayev et al. (2012)). Defect accumulation effect in the near surface region caused by MWT was reported in (Boltovets et al. (2002); Zayats et al. (2015)). To a certain extent only SIC3 sample was an exclusion, but in this case rather strong deformation of near surface region was also observed prior to irradiation. The researchers report (Bacherikov et al. (2003); Pashkov et al. (1994); Boltovets et al. (2002); Milenin et al. (1994); Belyaev et al. (2002)) that in this stressed state, MWT causes redistribution as well as certain weakening of elastic deformations, and this is what happens in SIC3. The profilometry data correlate with the results from X-ray measurements. The structure investigations show that dislocation density distribution across the area in the initial GaAs wafers is of W-like; the dislocation density over the plate diameter varied from $2 \cdot 10^4$ cm⁻² to $2 \cdot 10^5$ cm⁻². This inhomogeneity in dislocation density distribution is the evidence of considerably strong elastic deformations in the sample.

The performed analysis shows that ESC1 and ESC2 centers are complexes of silicon vacancies, EGA1 is associated with V_{As} , and EGA3 — with V_{As} or $V_{Ga}Ga_iV_{As}$ complex. MWT stimulated diffusion of point defects, which are mostly intrinsic interstitial atoms, results in trap modifications. ESC1 center in silicon carbide turns into ESC2 under the influence of closely located carbon interstitial:

$$V_{Si} V_C + V_{Si} V_C + C_i + C_i \rightarrow V_{Si} + V_{Si} \rightarrow V_{Si} V_{Si}$$
.

Further modification of ESC2 parameters in SIC3 is caused by the enhanced electric field of dislocation. In the samples of GAS2 at $t_{\rm MWT}=20~{\rm s},~{\rm V}_{\rm As}$ transforms into complex ${\rm V}_{\rm As}{\rm As}_i$ with which EGA2 center is associated, due to increased number of interstitial atoms in the near-surface layer:

$$V_{As} + As_i \rightarrow V_{Si} As_i$$
.

In GAS1 similar process is more complicated because of higher charge carrier concentration: it is reported (Zohm et al. (2000)) that with the growth of resistance the depth of microwave penetration grows and thus, the volume from which defect gettering begins in the near-surface layer grows as well. In addition, the

Table 2: Data reported for the levels close to detected levels

omplex with V_{As}	$, (E_c - E_t) =$	(0.51 - 0.52) ev	
			Diabtem et al. (2000)
- -	DLTS	no	Richter et al. (2000)
1/	DLTS	no	Neild et al. (1991)
V_{As}	LDA	no	Schultz (2015)
-	TSC	no	Pavlović et al. (2000)
-	DLTS	yes	Yousefi et al. (1995)
	DLTS	yes	Yousefi et al. (1995)
omplex with V _{As}	PA	no	Kuisma et al. (1997)
- As	TSC	no	Pavlović and Desnica (1998)
_	TSC	no	Tomozane and Nannichi (1986)
_	DLTS	no	Lang et al. (1976)
EGA2		$(0.28 \div 0.30) \text{ eV}$	Early et al. (1970)
$V_{As}As_i$	TSC	no	Pavlović et al. (2000)
$AS^{T}S_{l}$	DLTS		Yousefi et al. (1995)
-		yes	
-	TSC	no	Pavlović and Desnica (1998)
. . .	TSC	no	Pavlović and Desnica (1998)
intrinsic	TP	no	Abele et al. (1987)
-	DLTS	yes	Mircea and Mitonneau (1975)
omplex with Te	DLTS	no	Kol'chenko and Lomako (1994)
$V_{As}As_i$	DLTS	no	Pons and Bourgoin (1985)
E	$GA3, (E_c - E_c)$		roms and Bourgom (1966)
Sb_{Ga}	DLTS	no	Samoylov et al. (1994)
As_{Ga}^{++}	TSC	no	Pavlović et al. (2000)
¹ Ga			
- i	TSC	no	Pavlović and Desnica (1998)
impurity	TP	no	Abele et al. (1987)
-	DLTS	no	Martin et al. (1977)
-	DLTS	no	Lang et al. (1976)
V_{As} , $V_{Ga}Ga_iV_{As}$	DLTS	no	Pons and Bourgoin (1985)
EGA4	$\cdot, (E_c - E_t) =$	(0.39 - 0.41) eV	2 , ,
-	DLTS	no	Neild et al. (1991)
$V_{Ga}V_{As}$	DLTS	no	Samoylov et al. (1994)
$ m V_{Ga}Ga_{As}$	TSC	no	Fang et al. (1990)
-	DLTS	yes	Bourgoin et al. (1988)
-	SCRC	yes	Ashby et al. (1976)
_	DLTS	yes	Fang et al. (1987)
$V_{Ga}Ga_{As}$	DLTS	no	Vaytkus et al. (1988)
v Ga Ou _{As}	DLTS		Yousefi et al. (1995)
FGA5		yes (0.24 – 0.25) eV	10uscii et al. (1993)
LOAJ	DLTS	no	Neild et al. (1991)
	TSC		
-		no	Pavlović et al. (2000)
- 141 37	TSC	no	Lin et al. (1976)
omplex with V _{Ga}	TSC	no	Fang et al. (1990)
-	TSC	no	Tomozane and Nannichi (1986)
intrinsic	TP	no	Abele et al. (1987)
$V_{Ga}V_{As}$	DLTS	no	Morrow (1991)
$ m V_{Ga} m V_{As}$	DLTS	no	Bourgoin et al. (1988)
-	DLTS	yes	Mircea and Mitonneau (1975)
-	DLTS	no	Fang et al. (1987)
_	DLTS	yes	Yousefi et al. (1995)
EGA6	$(E_c - E_t) =$	(0.43 - 0.46) eV	1000011 01 01. (1770)
$V_{As}As_i, V_{As}$	TSC	no	Pavlović et al. (2000)
$A_{S}A_{S}$, A_{S}			
-	TSC	no	Pavlović and Desnica (1998)
intrinsic	DLTS	yes	Lefèvre and Schulz (1977)
		•	Bourgoin et al. (1988)
		yes	Kol'chenko et al. (1989)
spectroscopy; TS(C — thermali	ly stimulated curre	nt; LDA — local density approximation
	intrinsic complex with V _{As} spectroscopy; TS niques; TP — ph	omplex with V_{As} DLTS spectroscopy; TSC — thermall	•

7

cause of weak (in comparison with GAS2) influence of MWT on trap parameters in GAS1 is the absence of pressure stresses, which intensify MWT simulated complex formation process in the system's intrinsic defects. (see data for silicon carbide single crystals). In the GAT sample, which is also characterizes by a high concentration of free electrons, transformation of EGA3 to EGA4 ($V_{Ga}Ga_{As}$ complex) is going on in the reaction described in (Fang et al. (1990)):

$$V_{Ga} Ga_i V_{As} \rightarrow Ga_{Ga} V_{As} \rightarrow Ga_{As} V_{Ga}$$

Accumulation of a great number of interstitial atoms in the near-surface layer at high doses of radiation ($t_{\rm MWT} \approx 40~{\rm s}$ for gallium arsenide and $t_{\rm MWT} > 80~{\rm s}$ for silicon carbide) causes complete annihilation of vacancies (or transformation into antisite defects, whose levels are filled in the crystals with electron conductivity) and therefore TAV signal disappears (samples GAS1, GAS2, SIC1):

$$\begin{split} \text{SiC} & : \quad V_{\text{Si}} \ V_{\text{Si}} + \text{Si}_{i} + \text{Si}_{i} \rightarrow 0 \,; \\ \text{GaAs} & : \quad V_{\text{Si}} \ \text{As}_{i} \rightarrow 0 \,; \quad V_{\text{As}} + \text{Ga}_{i} \rightarrow \text{Ga}_{\text{As}} \,. \end{split}$$

It is believed (Abbate et al. (1995); Ostrovskii and Olikh (1998); Ostrovskii et al. (1998)), that TAV appearance in epitaxial structures is mostly caused by the defects located on the epi–layer and substrate interface. This difference in deep level location is the cause of the difference between dose-dependent modification of defect parameters in epitaxial and single crystal samples.

In epitaxial structures $n-n^+$ -GaAs and $n-n^+-n^{++}$ -GaAs, MWT induced increase of curvature radius reported in (Boltovets et al. (2002); Belyayev et al. (2012)) is the result of forming single dislocations and their further propagation deep into the structure along the glide planes. As a result, the strength of both electric and stress field changes, which causes defect transformation and thus the shift of respective deep levels. As seen from Table 2, the levels of EGA5 and EGA6 are associated with complexes V_{Ga}V_{As} and V_{As}As_i, respectively. Such traps as EGA2 and EGA4 have also been found in epi-structures before (Yousefi et al. (1995); Mircea and Mitonneau (1975); Bourgoin et al. (1988); Ashby et al. (1976); Fang et al. (1987); Lefèvre and Schulz (1977); Kol'chenko et al. (1989)). The observed MWT-stimulated transformations are caused by the growing number of interstitial atoms which are described by reactions like the following

$$V_{Ga} V_{As} + Ga_i + As_i \rightarrow V_{As} As_i$$

for GAE1 and GAE2 and

$$V_{Ga} Ga_{As} + As_i \rightarrow Ga_{Ga} V_{As} + As_i \rightarrow V_{As} As_i$$

for GAB1 and GAB2. The increase in activation energy EGA6 in sample GAE3 is caused, most probably, by the change in Coulombic interaction of interstitial—vacancy complexes which is due to decreased their concentration, while the growth of capture cross-section EGA4 in GAB1 at $t_{\rm MWT}=20~{\rm s}$ and EGA6 in GAE3 is associated with the growth of electric field strength caused by charged dislocations.

4. Conclusion

The influence of microwave radiation on the parameters of point defects (cross section of electron capture, energy levels in the gap) was studied experimentally in single crystals of n—6H—SiC and n—GaAs, as well as in gallium arsenide epitaxial structures. The investigation shows that the traps available in the near-surface layer are associated with the intrinsic vacancy-related defects. The microwave radiation induced change of the trap energy level as well as capture cross section is caused by the growing number of interstitial atoms in the near-surface layer. The radiation induced process involving the transformations of defect complexes are intensified in conditions of stresses.

CRediT authorship contribution statement

Oleg Olikh: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Review & Editing, Visualization. **Petro Lytvyn:** Conceptualization, Methodology, Validation, Resources, Writing - Original Draft.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was partially supported (O. Olikh) by National Research Foundation of Ukraine by the state budget finance (project number 2020.02/0036).

References

- Abbate, A., Ostrovskii, I.V., Han, K.J., Masini, G., Palma, F., Das, P., 1995. Transient acoustoelectric spectroscopy measurements for the characterization of GaAs epilayer structures. Semicond. Sci. Technol. 10, 965–969. doi:10.1088/0268-1242/10/7/011.
- Abele, J.C., Kremer, R.E., Blakemore, J.S., 1987. Transient photoconductivity measurements in semi-insulating GaAs. II. A digital approach. J. Appl. Phys. 62, 2432–2438. doi:10.1063/1.339476.
- Anikin, M., Andreyev, A., Lebedev, A., Pyatko, S., Rastegayeva, M.,
 Savkina, N., Strel'chuk, A., Syrkin, A., Chelnokov, V., 1991a.
 High temperature Schottky diode Au-SiC-6H. Fizika i tekhnika poluprovodnikov 25, 328–333. (in Russian).
- Anikin, M., Zubrilov, A., Lebedev, A., Strel'chuk, A., Cherenkov, A., 1991b. Recombination processes in 6H–SiC p–n–structures and the influence of deep centers. Fizika i tekhnika poluprovodnikov 25, 479–486. (in Russian).
- Ashby, A., Roberts, G., Ashen, D., Mullin, J., 1976. Non-extrinsic conduction in semi-insulating gallium arsenide. Solid State Commun. 20, 61–63. doi:10.1016/0038-1098(76)91699-9.
- Ashkinadze, B., Cohen, E., Ron, A., Linder, E., Pfeiffer, L., 1996. The effects of photogenerated free carriers and microwave electron heating on exciton dynamics in GaAsAlGaAs quantum wells. Solid-State Electron. 40, 561–565. doi:10.1016/0038-1101(95)00290-1.
- Bacherikov, Y., Konakova, R., Milenin, V., Okhrimenko, O., Svetlichnyi, A., Polyakov, V., 2008. Changes in characteristics of gadolinium, titanium, and erbium oxide films on the SiC surface under microwave treatment. Semiconductors 42, 868–872. doi:10.1134/S106378260807019.
- Bacherikov, Y.Y., Konakova, R.V., Kocherov, A.N., Lytvyn, P.M., Lytvyn, O.S., Okhrimenko, O.B., Svetlichnyi, A.M., 2003. Effect of microwave annealing on silicon dioxide/silicon carbide structures. Technical Physics 48, 598–601. doi:10.1134/1.1576474.
- Belyaev, A., Venger, E., Ermolovich, I., Konakova, R., Lytvyn, P., Milenin, V., Prokopenko, I., Svechnikov, G., Soloviev, E., Fedorenko, L., 2002. Effect of microwave and laser radiations on the parameters of semiconductor structures. Intac, Kyiv.
- Belyayev, A., Belyayev, A., Yermolovich, I., Komirenko, S., Konakova, R., Lyapin, V., Milenin, V., Solov'ev, E., Shevelev, M., 1998. Influence of microwave treatment on the electrophysical characteristics of technically important semiconductors and surface-barrier structures. Technical Physics 43, 1445–1449. doi:10.1134/1.1259222.
- Belyayev, A., Sachenko, A., Boltovets, N., Ivanov, V., Konakova, R., Kudryk, Y., Matveeva, L., Milenin, V., Novitskii, S., Sheremet, V., 2012. Effect of microwave irradiation on the resistance of Au–TiB_x–Ge–Au–n–n⁺–n⁺⁺–GaAs(InP) ohmic contacts. Semiconductors 46, 541–544. doi:10.1134/S1063782612040021.
- Bhunia, S., Bose, D., 1998. Microwave synthesis, single crystal growth and characterization of ZnTe. J. Cryst. Growth 186, 535–542. doi:10.1016/S0022-0248(97)00814-2.
- Boltovets, N.S., Kamalov, A.B., Kolyadina, E.Y., Konakova, R.V., Lytvyn, P.M., Lytvyn, O.S., Matveeva, L.A., Milenin, V.V., Rengevych, O.E., 2002. Microwave-stimulated relaxation of internal strains in GaAs-based device heterostructures. Technical Physics Letters 28, 154–156. doi:10.1134/1.1458520.
- Bourgoin, J.C., von Bardeleben, H.J., Stiévenard, D., 1988. Native defects in gallium arsenide. J. Appl. Phys. 64, R65–R92. doi:10.1063/1.341206.
- Bourgoin, J.C., De Angelis, N., 2001. The defect responsible for non-radiative recombination in GaAs materials. Semicond. Sci. Technol. 16, 497–501. doi:10.1088/0268-1242/9/2/005.
- Bulyarskii, S., Grushko, N., Zhukov, A., 2000. Field dependence of the rate of thermal emission of holes from the $V_{Ga}S_{As}$

- complex in gallium arsenide. Semiconductors 34, 40–44. doi:10.1134/1.1187958.
- Ermolovich, I., Milenin, G., Milenin, V., Konakova, R., Red'ko, R., 2007. Modification of the defect structure in binary semiconductors under the action of microwave radiation. Technical Physics 77, 1173–1177. doi:10.1134/S1063784207090113.
- Ermolovich, I.B., Venger, E.F., Konakova, R.V., Milenin, V.V., Svechnikov, S.V., Sheveljev, M.V., 1998. Photoluminescent investigations of SHF irradiation effect on defect states in GaAs:Sn(te) and InP crystals. Proc. SPIE 3359, 265–272. doi:10.1117/12.306225.
- Fang, Z., Shan, L., Schlesinger, T., Milnes, A., 1990. Study of defects in LEC–grown undoped SI–GaAs by thermally stimulated current spectroscopy. Materials Science and Engineering: B 5, 397–408. doi:10.1016/0921-5107(90)90104-J.
- Fang, Z.Q., Schlesinger, T.E., Milnes, A.G., 1987. Evidence for EL6 ($e_c-0.35$ eV) acting as a dominant recombination center in n-type horizontal Bridgman GaAs. J. Appl. Phys. 61, 5047–5050. doi:10.1063/1.338327.
- Godwod, K., Nagy, A.T., Rek, Z., 1976. The application of the x-ray triple-crystal spectrometer for measuring the radius of curvature of bent single crystals. Phys. Status Solidi A 34, 705–710. doi:10.1002/pssa.2210340235.
- Gromashevskii, V., Tatyanenko, N., Snopok, B., 2013. Application of the transverse acoustoelectric effect to studying silicon surface charging upon water adsorption. Semiconductors 47, 579–585. doi:10.1134/S106378261304009X.
- Hemmingsson, C.G., Son, N.T., Janzén, E., 1999. Observation of negative–U centers in 6H silicon carbide. Appl. Phys. Lett. 74, 839–841. doi:10.1063/1.123401.
- Kitchen, H.J., Vallance, S.R., Kennedy, J.L., Tapia-Ruiz, N., Carassiti, L., Harrison, A., Whittaker, A.G., Drysdale, T.D., Kingman, S.W., Gregory, D.H., 2014. Modern microwave methods in solid-state inorganic materials chemistry: From fundamentals to manufacturing. Chem. Rev. 114, 1170–1206. doi:10.1021/cr4002353.
- Kol'chenko, T., Lomako, V., 1994. New metastable center in irradiated GaAs. Fizika i tekhnika poluprovodnikov 28, 857–860. (in Russian).
- Kol'chenko, T., Lomako, V., Rodionov, A., Sveshnikov, Y., 1989. Features of defect formation in epitaxial gallium arsenide, which is containing isovalent indium impurity. Fizika i tekhnika poluprovodnikov 23, 626–629. (in Russian).
- Kozlovskii, V.V., Kozlov, V.A., Lomasov, V.N., 2000. Modification of semiconductors with proton beams. A review. Semiconductors 34, 123–140. doi:10.1134/1.1187921.
- Kuisma, S., Saarinen, K., Hautojärvi, P., Fang, Z.Q., Look, D., 1997. Microscopic nature of thermally stimulated current and electrical compensation in semi–insulating GaAs. J. Appl. Phys. 81, 3512– 3521. doi:10.1063/1.364705.
- Kuznetsov, N., Edmond, J., 1997. Effect of deep levels on current excitation in 6H–SiC diodes. Semiconductors 31, 1049–1052. doi:10.1134/1.1187023.
- Lang, D.V., Cho, A.Y., Gossard, A.C., Ilegems, M., Wiegmann, W., 1976. Study of electron traps in n–GaAs grown by molecular beam epitaxy. J. Appl. Phys. 47, 2558–2564. doi:10.1063/1.322974.
- Lebedev, A., Davydov, D., Tregubova, A., Bogdanova, E., Shcheglov, M., Pavlenko, M., 2001. Effect of structural imperfection on the spectrum of deep levels in 6H–SiC. Semiconductors 35, 1372–1374. doi:10.1134/1.1427973.
- Lebedev, A., Veinger, A., Davydov, D., Kozlovskii, V., Savkina, N., Strel'chuk, A., 2000. Radiation defects in n-6H-SiC irradiated with 8 MeV protons. Semiconductors 34, 861–866. doi:10.1134/1.1188089.
- Lebedev, A.A., 1999. Deep level centers in silicon carbide: A review. Semiconductors 33, 107–130. doi:10.1134/1.1187657.
- Lefèvre, H., Schulz, M., 1977. Double correlation technique

- (DDLTS) for the analysis of deep level profiles in semiconductors. Applied physics 12, 45–53. doi:10.1007/BF00900067.
- Lin, A.L., Omelianovski, E., Bube, R.H., 1976. Photoelectronic properties of high-resistivity GaAs:O. J. Appl. Phys. 47, 1852–1858. doi:10.1063/1.322904.
- Makram-Ebeid, S., Lannoo, M., 1982. Quantum model for phonon–assisted tunnel ionization of deep levels in a semiconductor. Phys. Rev. B 25, 6406–6424. doi:10.1103/PhysRevB.25.6406.
- Martin, G.M., Mitonneau, A., Mircea, A., 1977. Electron traps in bulk and epitaxial GaAs crystals. Electronics Letters 13, 191–193. doi:10.1049/el:19770140.
- Milenin, V., Konakova, R., Statov, V., Sklyarevich, V., Tkhorik, Y., Filatov, M., Shevelev, M., 1994. Physicochemical processes at the interface of contacts Au/Pt/Cr/Pt/GaAs, subjected to microwave annealing. Pis'ma v zhurnal tekhnicheskoy fiziki 20, 32–36. (in Russian).
- Mircea, A., Mitonneau, A., 1975. A study of electron traps in vapour–phase epitaxial GaAs. Applied physics 8, 15–21. doi:10.1007/BF00883664.
- Morrow, R.A., 1991. In–diffusing divacancies as sources of acceptors in thermally annealed GaAs. J. Appl. Phys. 69, 3396–3398. doi:10.1063/1.348519.
- Neild, S.T., Skowronski, M., Lagowski, J., 1991. Signature of the gallium–oxygen–gallium defect in GaAs by deep level transient spectroscopy measurements. Appl. Phys. Lett. 58, 859–861. doi:10.1063/1.104513.
- Nozariasbmarz, A., Dsouza, K., Vashaee, D., 2018. Field induced decrystallization of silicon: Evidence of a microwave non–thermal effect. Appl. Phys. Lett. 112, 093103. doi:10.1063/1.5020192.
- Olikh, O., Pinchuk, T., 2006. Acoustic wave corrected current-voltage characteristics of GaAs-based structures with Schottky contacts. Tech. Phys. Lett. 32, 517–519. doi:10.1134/S1063785006060204.
- Olikh, O.Y., Gorb, A.M., Chupryna, R.G., Pristay-Fenenkov, O.V., 2018. Acousto-defect interaction in irradiated and nonirradiated silicon n⁺-p structure. J. Appl. Phys. 123, 161573. doi:10.1063/1.5001123.
- Ostrovskii, I., Olikh, O., 1998. Characterization of interface deep levels in as vapor grown epi–GaAs. Solid State Commun. 107, 341–343. doi:https://doi.org/10.1016/S0038-1098(98)00236-1.
- Ostrovskii, I.V., Saiko, S.V., Walther, H.G., 1998. Determination of deep levels' parameters in epi–GaAs by a transient acoustoelectric technique. J. Phys. D: Appl. Phys. 31, 2319–2325. doi:10.1088/0022-3727/31/18/018.
- Pashkov, V., Perevoshchikov, V., Skupov, V., 1994. Influence of annealing in a microwave radiation field on the residual deformation and impurity composition of near-surface silicon layers. Pis'ma v zhurnal tekhnicheskoy fiziki 20, 14–18. (in Russian).
- Pavlović, M., Desnica, U.V., 1998. Precise determination of deep trap signatures and their relative and absolute concentrations in semi-insulating GaAs. J. Appl. Phys. 84, 2018–2024. doi:10.1063/1.368258.
- Pavlović, M., Desnica, U.V., Gladić, J., 2000. Complete set of deep traps in semi-insulating gaas. J. Appl. Phys. 88, 4563–4570. doi:10.1063/1.1308072.
- Pons, D., Bourgoin, J.C., 1985. Irradiation—induced defects in GaAs. J. Phys. C: Solid State Phys. 18, 3839–3871. doi:10.1088/0022-3719/18/20/012.
- Richter, T., Kühnel, G., Siegel, W., Niklas, J.R., 2000. Activation energies of the EL6 trap and of the 0.15 eV donor and their correlation in GaAs. Semicond. Sci. Technol. 15, 1039–1044. doi:10.1088/0268-1242/15/11/305.
- Samoylov, V.A., Yakusheva, N.A., Prints, V.Y., 1994. Effect of an isovalent antimony impurity on the formation of electrically active cents in *n*–GaAs obtained by liquid-phase epitaxy from a bismuth melt. Fizika i tekhnika poluprovodnikov 28, 1617–1626. (in Rus-

- sian).
- Schrimpf, R.D., Fleetwood, D.M., 2004. Radiation Effects and Soft Errors in Integrated Circuits and Electronic Devices. World Scientific. doi:10.1142/5607.
- Schultz, P.A., 2015. The E1–E2 center in gallium arsenide is the divacancy. J. Phys.: Condens. Matter 27, 075801. doi:10.1088/0953-8984/27/7/075801.
- Stellmacher, M., Bisaro, R., Galtier, P., Nagle, J., Khirouni, K., Bourgoin, J.C., 2001. Defects and defect behaviour in GaAs grown at low temperature. Semicond. Sci. Technol. 16, 440–446. doi:10.1088/0268-1242/16/6/304.
- Tomozane, M., Nannichi, Y., 1986. Improved thermally stimulated current spectroscopy to characterize levels in semi-insulating GaAs. Japanese Journal of Applied Physics 25, L273–L275. doi:10.1143/JJAP.25.L273.
- Vaytkus, Y., Storasta, Y., Pintsevichyus, A., Pyatrauskas, M., Kazhukauskas, V., 1988. Determination of the parameters of deep centers in semi-insulating GaAs from the relaxation of photoconductivity under laser excitation. Litovskiy fizicheskiy sbornik 28, 744–751. (in Russian).
- Yousefi, G.H., Webb, J.B., Rousina, R., Khanna, S.M., 1995. Electron irradiation induced defects and schottky diode characteristics for metalorganic vapor phase epitaxy and molecular beam epitaxial n– GaAs. J. Electron. Mater. 24, 15–20. doi:10.1007/BF02659720.
- Zayats, N.S., Konakova, R.V., Milenin, V.V., Milenin, G.V., Red'ko, R.A., Red'ko, S.N., 2015. Microwave-radiationinduced structural transformations in homo- and heterogeneous gaas-based systems. Technical Physics 60, 432–436. doi:10.1134/S1063784215030299.
- Zohm, H., Kasper, E., Mehringer, P., Müller, G., 2000. Thermal processing of silicon wafers with microwave co-heating. Microelectron. Eng. 54, 247–253. doi:10.1016/S0167-9317(00)00413-5.