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Modification of the Defect Structure in Binary Semiconductors under the Action of Microwave Radiation

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Abstract—Possible athermic processes caused by microwave processing (at $f = 2.45$ and 84 GHz) of semiconductors that influence their structure are analyzed. Models explaining the variation of the concentration of point and extended defects upon microwave irradiation are proposed. These models are qualitatively corroborated by experimental data for the structure and luminescence of semiconductors.

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INTRODUCTION

The unexpected effect of improvement of the electrical characteristics of Schottky diodes exposed to microwave radiation (the backward current and excessive forward current decrease, while the lifetime of minority carriers and their diffusion length grow) [1, 2] has given impetus to research concerning the influence of microwave radiation on the electrophysical parameters of semiconductors.

One could expect that, with process conditions chosen appropriately, microwave irradiation will be used as a specific procedure to improve the properties of semiconductor materials, e.g., homogenize their structure and eliminate unwanted effects.

In [3–5], associated studies were performed on silicon single crystals. Although the mechanism behind structural transformations observed in those works remained unclear, the assumption was made that microwave processing modifies the silicon structure by (i) altering the charge state of defects and (ii) inducing nonstationary elastic strain fields in the crystal, which result from instantaneous heating of its imperfect regions. It was shown, however, that the effects stimulated by microwaves cannot be explained by rapid thermal annealing alone. Presumably, athermic factors associated with specific features of microwave processing also play an important part in structural reconstruction.

In this work, we analyze athermic processes that may cause changes in the structure of semiconductors. Emphasis is on modification of binary semiconductors.

EXPERIMENTAL

Interaction between microwave radiation and semiconductors was studied by (i) taking photoluminescence spectra in the range 0.6–2.0 eV (photoluminescence was excited by light with $h\nu > 2$ eV and also using (ii) X-ray topography (the Borrmann method, CuK_α radiation), and (iii) X-ray diffraction to measure the radii of curvature of the samples.

Most measurements were made on n-GaAs wafers doped by Te and Sn. The concentration of free carriers in the samples was $(0.5–1.0) \times 10^{17}$ cm^{-3}.

The samples were exposed to directional radiation at $f = 2.45$ and 84 GHz under free-space conditions. The power of radiation sources was 100 W and 5 kW, respectively. The irradiation intensity was chosen such that heating of the samples was not too strong (≤100–150°C).

RESULTS AND DISCUSSION

X-ray topograms taken of as-grown GaAs wafers (Fig. 1a) showed that the material contains not only point defects and defect–impurity complexes, but also such structure imperfections as dislocations and microinclusions nonuniformly distributed over the wafers. All these imperfections may cause relaxation losses when the semiconductor material is exposed to microwave radiation and even lead to noticeable structural

† Deceased.

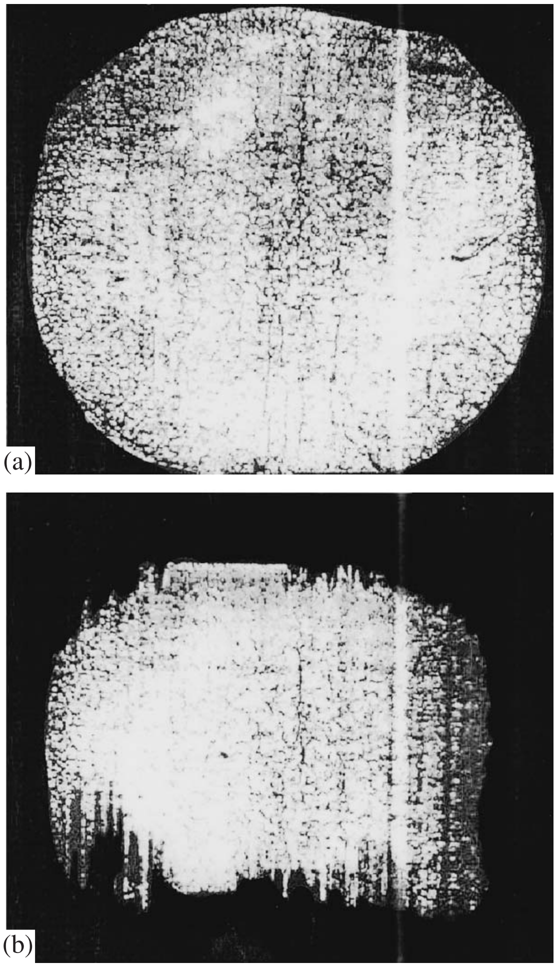

Fig. 1. X-ray topograms taken of GaAs wafers (a) before and (b) after microwave processing (f = 2.45 GHz, P = 100 W).

transformations if the radiation intensity is high enough (Fig. 1b).

To explain the results obtained, we will employ a mechanism of dislocation multiplication that is based on the Frank–Reed multiplication model [6–8]. In this model, a dislocation (Frank–Reed source) is fixed by some barriers on both ends. At certain critical shear stress τ_c, a dislocation loop is generated and a new dislocation appears. This process may be repeated many times when

$$\tau_c = \frac{Gb}{L}, \tag{1}$$

where G is the shear modulus, b is the Burgers vector, and L is the dislocation length.

Dislocation loops may be generated under the action of both mechanical and electrostatic forces if the original dislocation has an uncompensated charge. In fact, generation of dislocations is accompanied by the appearance of dangling bonds. For distance C between dangling bonds as a function of angle α between the dislocation line and Burgers vector, Reed derived the expression [8]

$$C = 0.866 b \operatorname{cosec} \alpha. \tag{2}$$

The electron of a dangling bond may leave an edge dislocation or be captured by it, which changes the charge state of the dislocation. The critical electric field causing generation of dislocation loops can be calculated from the expression

$$E_c = \frac{Cb^2c}{qL}, \tag{3}$$

where q is the electron charge.

If a dislocation segment is subjected to the joint action of mechanical and electric fields, the expression for E_c takes the form

$$E_c = \frac{Cb}{q}\left(\frac{Gb}{L} - \tau\right). \tag{4}$$

Let us estimate field intensity E_c necessary for generation of dislocation loops. It is assumed that a segment of an edge dislocation with $L = 10^6 b$ is present in a GaAs layer and the Burgers vector of the dislocation is equal to lattice constant $d = 5.65 \times 10^{-10}$ m. Shear modulus G in the $\langle 100 \rangle$ direction at temperature T = 300 K equals 60 GPa [9]. If $C = 0.866b$ for the edge dislocation, calculation by formula (4) yields $E_c = 1 \times 10^8$ V/m.

If the semiconductor structure is under mechanical stress $\tau \approx 50$ MPa, which acts upon the dislocation segment, calculations by formula (4) yield $E_c = 1.7 \times 10^7$ V/m. Such an electric field can be provided, in general, by only electromagnetic sources based on high-current relativistic electron accelerators or, in our case, only on gyrotrons operating under extreme conditions (f = 84 GHz). Therefore, additional factors influencing E_c in the course of microwave processing should be taken into account.

As before, we will consider a dislocation as a string to which an external (driving) force varying by a harmonic law is applied at a certain point,

$$F = F_0 \sin \omega t.$$

Then, the amplitude of forced oscillations can be written as [10]

$$V(x, t) = -\frac{2\omega F_0}{L\rho}\sum_{n=1}^{\infty}\frac{1}{\omega_n}\frac{\sin\frac{n\pi c}{L}}{\omega_n^2 - \omega^2}\sin\omega_n t \sin\frac{n\pi x}{L} + \frac{2F_0}{L\rho}\sin\omega t\sum_{n=1}^{\infty}\frac{\sin\frac{n\pi c}{L}}{\omega_n^2 - \omega^2}\sin\frac{n\pi x}{L}, \tag{5}$$

where ω is the frequency of the external force, $F_0 = QE$ is the amplitude of the driving force, $\omega_n = an\pi/L$ is the free oscillation frequency of the string, $a = \sqrt{T_0/\rho}$ is the velocity of oscillation propagation, $T_0 = Gb^2$ is the linear tension of the string [7], and ρ is its linear density ($\rho = zA/N_A d$, where A is the atomic weight, N_A is the Avogadro number, d is the lattice constant, and z is the number of atoms per unit cell).

The first term in Eq. (5) describes the free oscillations of the string. The second one, having the same frequency as the frequency of the field-induced driving force, becomes very large when ω approaches the free oscillation frequency of the string; i.e., a resonance takes place.

When the driving force is applied exactly to the midpoint of the string ($L/2$), its related oscillation component has the form

$$\nu(x, t) = \frac{2F_0}{L\rho}\sin\omega t\sum_{n=1}^{\infty}\frac{\sin\dfrac{n\pi}{2}}{\omega_n^2-\omega^2}\sin\frac{n\pi x}{L}. \qquad (6)$$

Multiple generation of dislocation loops by a Frank–Reed source occurs when the amplitude of forced oscillations exceeds $L/2$ [7].

When ω approaches one of ω_n, the condition for generation of dislocation loops becomes

$$E_c = \frac{L^2\rho(\omega_n^2-\omega^2)}{4Q\sin^2 n\pi/2}. \qquad (7)$$

Let us estimate E_c for various frequencies of the electromagnetic wave. First, we will calculate ω_n for a dislocation segment with $L = 10^3 b$. Taking into account that $A = 144.64 \times 10^{-3}$ kg and $z = 8$ for GaAs and also that $N_A = 6.02 \times 10^{23}$ mol^{-1}, we find that $\rho = 3.4 \times 10^{-15}$ kg/m, $T_0 = 1.92 \times 10^{-8}$ N, and $a = 2.38 \times 10^3$ m/s. Accordingly, $\omega_n = 13.23n$ GHz. Further, we will use the lowest frequency, $\omega_1 = 13.23$ GHz.

Let us now estimate E_c for situations in which $\Delta\omega = \omega_n - \omega$ equals 1 GHz, 100 MHz, and 10 MHz. According to Eq. (8), we obtain, respectively, $E_c = 4.0 \times 10^7$, 4.0×10^6, and 4.0×10^5 V/m; i.e., the critical field necessary for generation of dislocation loops declines with decreasing frequency.

The behavior of the dislocation segment in a high-frequency electric field may be strongly affected by impurity atoms, which decorate dislocations. Having accumulated at dislocations, they, on the one hand, raise ρ and thereby decrease frequency ω_n; on the other hand, impurity atoms may detach from dislocations at high oscillation amplitudes and free impurity atoms may appear in the crystal.

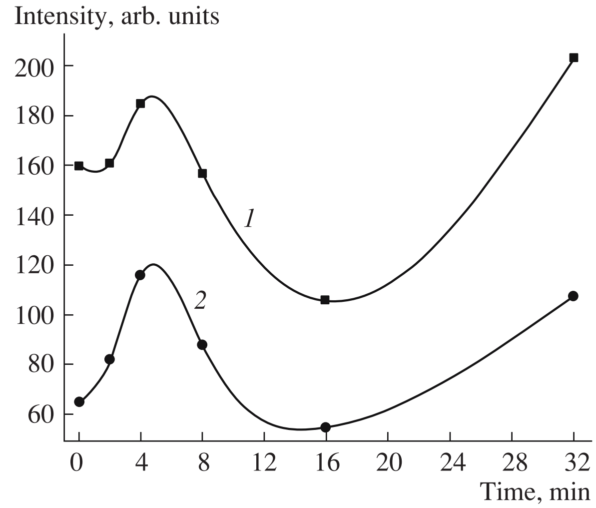

Fig. 2. Photoluminescence intensity in samples with a vicinal surface (deviation from (100) is a') vs. the microwave processing duration ($f = 2.45$ GHz, $P = 100$ W): (*1*) 1.18 and (*2*) 1.10 eV.

The dielectric losses of the resonance current in the course of microwave processing may also play an important part in reconfiguring local centers produced by point defects and/or their complexes.

Indeed, it is known that local centers in III–V compounds may execute microwave oscillations [11]. These centers are vacancy–impurity associations and are characterized by strong electron–phonon bonds. An increased concentration of these centers in crystals results from various active (radiation, thermal, etc.) actions, processes at semiconductor–metal interfaces, and so on. The transitions of electrons to the energy levels of such centers may involve phonon modes. These features of electron oscillation centers may exert an effect on the absorption and luminescence spectra of crystals that contain these centers, because their metastable excited states may take part in absorption and luminescence. Finally, if the electric field frequency equals the eigenfrequency of defect oscillations, the migration probability of defects increases. Defects may migrate not only within the neighborhood but also cover long distances, and migration may be accompanied by breakage of the initial chemical bond. It is clear that transitions of this type do not require much energy and the ultimate result of microwave action on a semiconductor depends on its composition and structure (presence of inhomogeneities).

Analysis of the resonance absorption spectra with allowance for interaction between the oscillator and ambient medium [12] shows that the actual frequency of resonance absorption differs from resonance absorption frequency ω_r evaluated with neglect of attenuation

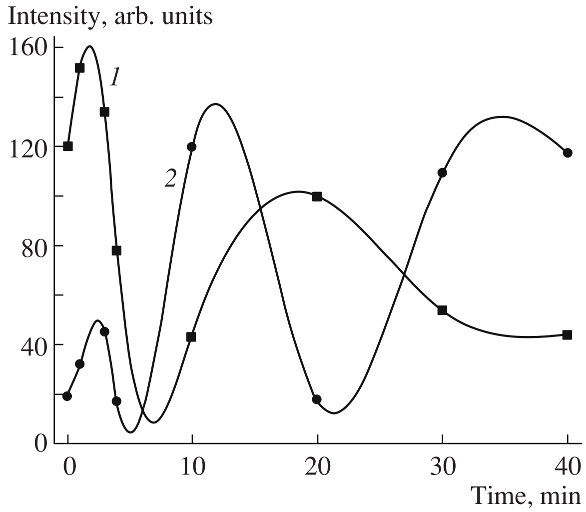

Fig. 3. Photoluminescence intensity for Sn-doped (100)GaAs samples vs. the microwave processing duration (f = 84 GHz, P = 5 kW): (*1*) 1.01 and (*2*) 1.28 eV.

(or polarization of the ambient medium),

$$\omega_r = \sqrt{\omega_0^2 - \frac{N^2 q^2}{m}}, \tag{8}$$

where N and m are the concentration of defects and mass of a defect.

Below, we focus on the experimental results that may serve as a physical validation of the above models. Figure 1 shows X-ray topograms taken of two n-(100)GaAs wafers with free carrier concentration $n = 3 \times 10^{16}$ cm^{-3}. It is seen that microwave processing in free space ($f = 2.45$ GHz, $P \leq 100$ W) changes the original structure of the semiconductor, namely, facilitates generation of dislocations and shrinks point defect clusters. The observed structural transformations are presumably of an oscillatory character, because residual strain relaxation, which reflects the variation of these transformations, is also oscillatory.

These results corroborate the data for residual strain relaxation in 350- to 400-μm-thick silicon wafers [5]. It was found that this process differs significantly from standard thermal annealing and exhibits a complex oscillating behavior with clearly pronounced athermic regions (an activation energy of ≤0.065 eV). Both annealing techniques give the same results only when exposure to microwaves suffices to heat up the semiconductor to a temperature of ≥400°C.

It was found [13] that exposure to microwave radiation with an energy density of 1.5 W/cm^2 for ≤10 s (which is evidently insufficient to heat up a structure formed by a quasi-amorphous TiB_x layer and GaAs) produces a periodic contrast in the form of parallel bands in the (111) direction. It is also worth noting that the radius of curvature of these structures is an oscillating function of the irradiation time (see table).

Radius of curvature of the TiB_x–n-GaAs–n^+-GaAs structure vs. the microwave irradiation time

t, s	0	0.5	1.5	3.5	6.0	9.0	13.0	18.0
R, m	7.5	6.0	5.4	12.2	15.1	11.1	11.7	6.7

To find out basic mechanisms underlying a change in the defect subsystem of the semiconductor upon microwave processing and to verify the models proposed needs detailed data for the type of defects, including the parameters of their clusters. This is a challenging problem, the solution of which requires a complex experimental approach. Associated difficulties have not yet overcome.

The athermic mechanisms of restructuring considered above do not describe the entire variety of processes occurring in the nonequilibrium defect structure of single-crystal semiconductors in the course of microwave processing. One of them is the oscillatory variation of the photoluminescence line intensity with exposure time, as revealed in our study. Such a dependence is exemplified in Fig. 2. Here, we observe the symbate variation of the photoluminescence intensity with exposure duration. These results can be interpreted in simple terms. It was shown [14] that microwave radiation causes a synergetic response of samples to this action. As a result, background impurities (and, perhaps, defects), which initially were distributed over the volume uniformly, acquire a banded distribution with a fixed period. These impurity centers or their complexes may serve as centers of nonradiative recombination, which is the reason for the oscillatory behavior of the photoluminescence intensity.

However, the real situation is much more complex. Although the photoluminescence intensity does oscillate in space and time, the behavior of individual lines is not most often symbate (Fig. 3).

The effects observed may be due to the fact that, when an ensemble of lattice defects configures into a spatially regular (periodic) dissipative structure, this structure gives rise to an additional channel for electromagnetic energy redistribution, along with the solid-state matrix (atomic regularity), and thereby provides a variety of processes of nonequilibrium defect self-organization in solids.

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