The Experimental Proof of Non-Thermal Nature of the Mechanism of Pulse-Photon Annealing in Semiconductor Materials

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Abstract. Nanosecond laser annealing of GaAs amorphized with B⁺ ions implantation was investigated. The recrystallization process observed in the experiment does not depend on the initial temperature of the samples (77K or 300K) and can be additive; the efficiency of laser annealing (LA) is determined by the light generated nonequilibrium charge carriers (NCC) rather than by crystal heating; the results of the experiments cannot be explained by the purely thermal mechanism of LA. The hypotheses for the low-temperature LA of semiconductors based on the concept of the change in the quantum state of valence electrons affecting a chemical bond are proposed. If the power of LA ensures light generation of antibonding quasiparticles with a concentration of \( n_{cr} \) in the thickness equal to or greater than the amorphous (defective) layer, melting occurs with further epitaxial growth on the substrate, which agrees well with the results of the experiment where the concentration of light generated NCC was \( \Delta n \approx 4.5 \cdot 10^{19} \text{cm}^{-3} \).

1. Introduction

As is known, one of the main methods of modifying the physical properties of semiconductor materials is impurity doping by ion implantation.

During ion implantation, a large number of radiation defects strongly affecting the physical properties of a semiconductor are formed. The solution to this problem by a high-temperature thermal annealing does not yield any desired results. Heating with partial annealing of defects leads to their transformation into other more complex defects, and a considerable part thereof remains in the crystal until high temperatures are achieved. High temperatures, in their turn, cause irreversible changes in the physical properties of the starting material.

So-called “Laser Annealing” appeared to be the most effective way to eliminate defects. Short-term exposure of ion-implanted semiconductor layers to electromagnetic waves turned out to be sufficient for more efficient annealing of radiation defects than thermal annealing in the furnace. It is very important for modern electronic technologies with nanoscale film thicknesses.

Annealing of defects in semiconductors is an activation-diffusion process and is determined by temperature and time. Hence, a decrease in the annealing time will certainly require an increase in
temperature. In most experiments, LA is performed with nanosecond pulses. Estimates have shown [1-7] that for such short durations of light exposure the layer melting is necessary for effective elimination of radiation defects. Thus, the physical LA mechanism comes down to understanding the mechanism of the process of melting of the defect layer of a semiconductor material.

The currently available models of pulsed laser annealing can be divided into two groups: thermal (heat) and nonthermal (ionization) models.

The thermal model means that the light energy absorbed by the material due to nonradiative recombination (mainly Auger recombination) is transferred to the lattice in the thin surface layer, the size of which is determined by the absorption coefficient of the material. This results in the rapid (~10^{10} \text{Ks}^{-1}) heating of the layer, which leads to its melting.

The main criterion for understanding the LA mechanism is how far the conditions of the proposed theoretical models can be realized experimentally. These criteria for the thermal LA mechanism are the temperature and the duration of the crystal heating process.

Today, the majority of scientists engaged in this field believe that the pulsed LA is the way to rapidly heat the sample, and the efficiency of the process depends on the factors determining heating of the material - the temperature and the duration of the process.

However, there are a number of experiments that cannot be explained by the thermal mechanism, since the energy transmitted by a laser pulse in a thin defect layer of a semiconductor material is insufficient for heating up to the melting point [1-3].

2. Experiment and Results

Studies were carried out on Zn-doped p-GaAs samples, at a concentration of $p = 10^{18} \text{cm}^{-3}$, with an orientation of (100). The samples were implanted with B+ ions with the energy of 40 keV, the dose of $6.25 \times 10^{15} \text{cm}^{-2}$. The average projected ion path was $R_p = 0.0956 \mu\text{m}$. As a result of irradiation, the amorphization of the surface layer was achieved. Laser annealing (LA) was carried out ($\lambda = 0.69 \mu\text{m}$, $\tau_p = 4 \times 10^{-8}\text{s}$), both in air, at the initial temperature of the sample $T_{in} = 300 \text{K}$, and in liquid nitrogen ($T_{in} = 77 \text{K}$). The laser beam fell perpendicularly onto the amorphized surface of the sample through the window of an optical Dewar vessel. Electron diffraction patterns of the samples irradiated with a different number of laser pulses were taken. The duration between pulses was 3-5 min.
Figure 1. Electron diffraction patterns of samples subjected to: laser irradiation \((T_{in} = 77 \text{ K}, E = 0.2 \text{ J/cm}^2)\) with one pulse (Figure 1a), 3 pulses (Figure 1b), 5 pulses (Figure 1c); laser irradiation \((T_{in} = 300 \text{ K}, E = 0.2 \text{ J/cm}^2)\) with 5 pulses (Figure 1d); laser irradiation \((T_{in} = 77 \text{ K}, E = 5 \text{ J/cm}^2)\) with one pulse (Figure 1e); laser irradiation \((T_{in} = 300 \text{ K}, E = 5 \text{ J/cm}^2)\) with one pulse (Figure 1f).

Figure 1a, 1b and 1c shows electron diffraction patterns of samples subjected to laser irradiation \((T_{in} = 77 \text{ K}, E = 0.2 \text{ J/cm}^2)\) with one pulse (Figure 1a), 3 pulses (Figure 1b) and 5 pulses (Figure 1c). As can be seen, after one and three pulses, the beginning of the recrystallization process is not yet noticeable, and after five pulses, a transition of the amorphous state to the polycrystalline state is observed. A similar experiment was conducted on samples with \(T_{in} = 300\text{K}\). The results were identical. The process of nucleation of a polycrystalline structure also manifested itself only after five laser pulses (Figure 1d). A further increase in the number of pulses, regardless of the initial temperature of the sample, did not lead to the transition of the polycrystalline state to the single crystal state. The second series of experiments was carried out at higher laser pulse energies \((E = 5 \text{ J/cm}^2)\). As in previous experiments, the LA process proceeded equally regardless of the initial sample temperature. However, the first laser pulse, in contrast to the previous experiment, led to the nucleation of a polycrystalline structure (Figure 1e, 1f). A further increase in the number of pulses also did not cause a transition to a single crystal state. The increase in the LA energy density \((at T_{in} = 300\text{K})\) was limited by the onset of the destruction of the surface layer.

For comparison, part of the samples was subjected to thermal annealing (TA) in vacuum at temperatures of \(373 \div 1073\text{ K}\), under protective Si$_3$N$_4$ films. As shown by the TA studies, a significant change in the structural properties of amorphous gallium arsenide was observed at \(T > 973\text{K}\).

In order to judge the LA mechanism, it is necessary to estimate the concentration of nonequilibrium charge carriers and the crystal heating temperature. In [2, 3], it was shown that in gallium arsenide with a high generation rate, a decrease in the concentration of NCC is determined by radiative recombination. This is true only for relatively lightly doped GaAs, not exposed to radiation. When GaAs is irradiated with high-energy particles, radiation defects are created in the material, which are centers of non-radiative recombination. In this case, the effective lifetime of free charge carriers will be determined by Auger recombination.
To estimate the concentration of NCC in our experiments, we use the formula:

\[
\frac{d(\Delta n)}{dt} = G - \frac{\Delta n}{\tau} - \gamma(\Delta n)^3 + D_a \frac{\partial^2 (\Delta n)}{\partial x^2}
\]

(1)

Where \( \tau \) is the carrier lifetime due to recombination at deep levels, \( \gamma \) is the Auger recombination coefficient, \( D_a \) is the ambipolar diffusion coefficient, \( G \) is the generation rate, determined by the intensity of the incident radiation. In the process of LA, the stationary concentration of NCC is realized, i.e. \( \frac{d\Delta n}{dt} = 0 \). At low generation rates, a decrease in the concentration of NCC will be determined by the second member of the right side of equation 1, and at high rates - by the third member. Auger recombination will dominate when \( \gamma(\Delta n)^3 > \frac{\Delta n}{\tau} \), where \( \gamma = 3 \cdot 10^{-31} \text{ cm}^6 \text{ s}^{-1} \), and \( \tau \) is the NCC lifetime determined by recombination at deep level centers. Under the experimental conditions, \( \tau \approx 10^{-11} \text{s} \). Then we get that \( \Delta n > \left( \frac{1}{\gamma} \right)^{\frac{1}{3}} = 6 \cdot 10^{20} \text{ cm}^{-3} \). To ensure such a NCC concentration, it is necessary to fulfill the condition \( G \geq \gamma(\Delta n)^3 \). Let us estimate the value of \( G \) under the conditions of this experiment according to the formula:

\[
G = \frac{(1 - R)E \alpha}{\hbar \nu \tau_i}
\]

(2)

where, \( R \) is the reflection coefficient, \( \alpha \) is the absorption coefficient, \( W \) is the energy density of the laser pulse, \( \tau_p \) is the laser pulse duration, \( h\nu \) is the photon energy of laser radiation; with \( T_m = 300 \text{K}, R = 0.4, \alpha = 10^5 \text{ cm}^{-1}, h\nu = 1.79 \text{ eV}, \tau_1 = 4 \cdot 10^4 \text{ s}, E_1 = 0.2 \text{ J/cm}^2 \) and \( E_2 = 10 \text{ J/cm}^2 \). The simplest calculation gives \( G_1 = 10^{26} \text{ cm}^3 \text{ s}^{-1} \) and \( G_2 = 2 \cdot 10^{28} \text{ cm}^3 \text{ s}^{-1} \). It can be seen that for the realized LA mode, the generation rate is substantially less than the value at which Auger recombination dominates. Therefore, the stationary concentration of NCC \( \Delta n_o \) will be determined by the 1st and 2nd members of the right side of equation 1 (the 4th member does not make a significant change in the \( \Delta n \) value). From this it follows that \( \Delta n_o = G \tau \) and therefore \( \Delta n_1 = 10^{13} \text{ cm}^{-3}, \Delta n_2 = 2 \cdot 10^{15} \text{ cm}^{-3} \). The allowance for differences in the values of \( R, \alpha, \) and \( \tau \) at \( T_m = 77 \text{ K} \) does not lead to a noticeable change in the value of \( \Delta n \).

The value of thermal heating was estimated using the method outlined in [2], under the following assumptions: the specific gravity \( \rho = 5.3 \text{ g/cm}^3 \); heat capacity \( C = 0.35 \text{ J/gK} (300 \text{ K}) \) and \( 0.167 \text{ J/gK} (80 \text{ K}) \); thermal conductivity coefficient \( \alpha = 0.55 \text{ W/cmK} (300\text{K}) \) and \( 2.7 \text{ W/cmK} (77\text{K}) \); melting point \( T_{melt} = 1511 \text{ K} \).

As the calculations showed, at the initial temperature of the crystal of 77K, in order to reach a temperature of \( \sim 1073 \text{ K} \) on the surface of the implanted GaAs layer, it is necessary to spend 1.5 times more light energy than at the temperature of 300K. In the experiment, in the process of LA, the temperature increment is:

- \( \Delta T \approx 5-7 \text{ K} \) at the laser pulse energy \( E = 0.2 \text{J/cm}^2 \) and temperatures \( T_{in} = 77-300 \text{K} \);
- \( \Delta T \approx 500 \text{ K} \) at \( E = 5 \text{J/cm}^2 \) and \( T_{in} = 77 \text{K} \);
- \( \Delta T \approx 750 \text{K} \) at \( E = 5 \text{J/cm}^2 \) and \( T_{in} = 300 \text{K} \).

A similar experiment was conducted with nanosecond pulse LA (\( \lambda = 0.69 \text{ \mu m}, E = 5 \text{J/cm}^2, \tau = 35 \text{ ns} \)). After the first pulse, regardless of the initial temperature of the sample (77 or 300 K), complete recrystallization of the amorphized layer is observed. Estimates of temperatures from the thermal LA
model show: for \( T_{in} = 300K \), \( T \approx T_{melt} \) and for \( T_{in} = 77K \), \( T \approx 0.7T_{melt} \). Regardless of \( T_{in} \), the concentration of light generated NCC was \( \Delta n \approx 4.5 \times 10^{19} \text{cm}^{-3} \).

Thus, we have obtained that: the recrystallization process observed in the experiment does not depend on the initial temperature of the samples (77K or 300K) and can be additive; the efficiency of LA is determined by the light generated NCC rather than by crystal heating; the results of the experiments cannot be explained by the purely thermal mechanism of LA.

3. Discussions
The main criterion for nonthermal LA models is the agreement between the theoretical and experimental values of the ionization level. In [1], a model of "plasma annealing" is proposed where it is assumed that under the action of short laser pulses the excitement and heating of the electron-hole plasma takes place. In this case, the lattice atoms remain relatively cold. The breaking of a large number of atomic bonds leads to the loss of the amorphous layer stability. The crystallization process is a second-order transition without the melting process. However, for the realization of this mechanism, the degree of ionization of \( 8 \times 10^{21} \text{cm}^{-3} \) must be achieved. According to the authors, such high levels of excitation can be achieved only at femtosecond pulses of a laser [1, 8, 9].

In [3] the hypotheses for low-temperature LA of semiconductors based on the concept of the change in the quantum state of valence electrons affecting a chemical bond was proposed. The electron transition from the valence band (bonding state) to the conduction band (antibonding state) results in the birth of two antibonding particles - an electron in the conduction band and a hole in the valence band, and hence, in the modification of the force and the type of bonding (isotropy of bonds). For example, in semiconductors with the diamond structure (Ge, Si, etc.) and in the \( A^3B^5 \) compounds (GaAs, etc.) the electrons transfer from the bonding \( p \)-state in the valence band (directed valences) to the antibonding symmetric state - \( s \) in the conduction band. In this work, the existence of some critical concentration \( n_{cr} \), such that, if the density of the antibonding quasi-particles is \( n > n_{cr} \), the initial state of the semiconductor can become unstable, seems absolutely natural. In contrast to the bonding electrons in a covalent bond when a pair of electrons is collectivized between two neighboring atoms, the antibonding quasi-particle weakens bond not only locally at any lattice site, but in the entire region of its delocalization, i.e. in the region with the sizes of its de Broglie wavelength. As showed calculation [3], the critical concentrations for GaAs crystallization equal \( 3.0\times 10^{18} \text{cm}^{-3} \).

Based on the foregoing, it follows that if the power of LA ensures light generation of antibonding quasiparticles with a concentration of \( n_{cr} \) in the thickness equal to or greater than the amorphous (defective) layer, melting occurs with further epitaxial growth on the substrate, which agrees well with the results of the experiment where the concentration of light generated NCC was \( \Delta n \approx 4.5 \times 10^{19} \text{cm}^{-3} \). At \( \Delta n < n_{cr} \), when the melting condition is not created in the entire defect region, the crystallization process can begin in the areas of the most intense recombination of electron – hole pairs, which is the amorphous phase – crystal interface. Due to fluctuations in the carrier concentration, in local places at the interface (or in the most defective area), there may be places with increased density of antibonding quasiparticles, sufficient to carry out melting with the formation of crystal nuclei. The higher the concentration of light generated antibonding quasiparticles, the greater will be the size or concentration of crystal nuclei.

4. Conclusions
To summarize, the results of the experiments showed that: the melting is achieved at temperatures significantly lower than the temperature required by the thermal LA model; the main criterion for the "cold" melting at LA is the value of the concentration of the light-generated antibonding quasiparticles. The above considerations suggest that during LA, when in order to achieve total RD annealing, melting of the material is required, the concentration of light-generated NCC is crucial.
rather than the thermal heating. We believe that the possibility of low temperature LA in semiconductors according to the theoretical model proposed in this paper has been proved experimentally.

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