Effect of infrared laser radiation on the structure and electrophysical properties of undoped single-crystal InAs

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Substantial changes have been found in the electrical properties and structural parameters of singlecrystal InAs after exposure to infrared laser radiation with photon energy less than the energy gap of InAs and power density $W < 50 \text{ W/cm}^2$. The changes are due to the transformation and redistribution of intrinsic point defects in the field of the laser electromagnetic field. © 1997 American Institute of Physics. [S1063-7826(97)01510-X]

1. INTRODUCTION

One of the effective ways of controlling a semiconductor is to expose it to laser radiation which modifies its surface properties ($\hbar \omega > E_g$) (Ref. 1) or bulk properties ($\hbar \omega < E_g$) (Ref. 2), depending on the ratio of the laser photon energy $\hbar \omega$ to the energy gap E_g . However, despite many attempts, the mechanism responsible for the interaction between laser radiation and crystals has not yet been fully elucidated. We have therefore undertaken an investigation of laserstimulated ($\hbar \omega < E_g$) transformation of structural and electrical properties of InAs crystals with a narrow homogeneity interval and a narrow energy gap.

2. EXPERIMENTAL METHOD

We used continuous CO₂-laser radiation with $\hbar \omega = 0.0018$ eV. The transport coefficients were measured by standard methods and the stoichiometry of the samples was monitored by X-ray diffraction methods, using quasi-forbidden reflections.³ This method is sensitive to changes in the sample and, if the intensity of the diffracted X-rays can be measured to better than 0.3%, it can be used to monitor changes in composition at the level of 10^{17} cm⁻³. The change in the integrated intensity ΔR_1 is related to the change in the concentration c_i by

$$\Delta R_i / R_i = k(c_{\rm ln} - c_{\rm As}), \tag{1}$$

where the constant k depends on the type of reflection and the form of radiation. Calculations show that for $CuK\alpha 1$ radiation and the (222) reflection, the difference $c_{In}-c_{As}$ can be detected at the level of 1.2×10^{-4} . The change in the relative volume fraction of the distorted lattice, ρ_0 , was determined by measuring the increase in the integrated intensity due to the diffuse component of scattering by distortions in the (333) reflection, using the formula⁴

$$R_{ie} = (1 - \rho_0) R_D + \rho_0 R_K, \qquad (2)$$

where $R_{ie}R_D$, R_K are the integrated intensities, respectively, measured and calculated from the dynamic and kinematic models of scattering.

We investigated undoped single-crystal InAs. The samples were cut from a single ingot and were polished and etched in order to remove the surface layer. The crystals had near-stoichiometric composition with a slight tendency toward the excess of As atoms or the metal component, and had *p*- and *n*-type conductivity, respectively.

3. RESULTS AND DISCUSSION

Samples cut from a single-crystal bulk plate were found to have different types of conductivity at 77 K. The carrier concentration in *n*-type samples was practically independent of temperature down to the region of instrinsic conduction. At low temperatures, the degree of concentration was probably determined by electroactive intrinsic defects, lying deep in the conduction band, so that they were not seen in the temperature dependence of the Hall constant R_H or the conductivity σ . Samples of the second type, whose conductivity at 77 K was $\sigma_{77}=0.25\times10^{-1}$ Om⁻¹ cm⁻¹, had $R_H(T)$ typical for *p*-typical samples, i. e., the conduction type is inverted as the temperature is increased (T=240-250 K). For *n*-type conduction, the behavior of the Hall coefficient $R_H(T)$ is the same as in the first case.

The samples were then exposed to the laser radiation $(\hbar \omega = 0.118 \text{ eV}, E_g = 0.35 \text{ eV}, \hbar \omega < E_g)$. For low power densities $(W1 = 10 \text{ Wcm}^2)$, the measured concentration of electrons in type-1 samples decreases slightly with exposure time. An increase in the power density to $W_2 = 20 \text{ W/cm}^2$ produces an appreciable rise in carrier concentration for a shorter exposure time as compared with W_1 . Further exposure under the same conditions leads to a monotonic reduction in electron concentration to below the initial level (Fig. 1). The carrier mobility at T=77 K was found to increase during the exposure of the crystals to the laser radiation, and eventually exceeded the initial value by a factor of 2.

X-ray studies suggest that all this is accompanied by a change in the distribution of InAs atoms in the lattice. The integrated intensity R_i at first decreases from its initial value corresponding to a surplus of In atoms. This continues almost down to the stoichiometric value (Fig. 2), but then rises with increasing power density W_2 to a level greater than the initial value. Continuing exposure with W_2 = const leads to a reduction in R_i below the level corresponding to the stoichiometric value (excess An).

In *p*-type crystals, the low power density $W_1 = 15$ W/cm² does not induce appreciable changes at room temperature, whereas at 77 K the hole concentration at first increases with time, but then tends to saturate (Fig. 3). As the

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FIG. 1. Ratio of Hall coefficients R_L/R_0 as a function of exposure to the infrared radiation for InAs samples with excess In. R_0 is the Hall coefficient prior to exposure.

power density increases $(W_1 < W_2)$, the hole concentration rises rapidly in a time t=30 min, followed by a fall with increasing exposure time. When the power density is then increased to $W_2 = 25$ W/cm², the samples undergo a transition to the state with *n*-type conductivity and anomalously high mobility at 77 K $\mu_{77} = 6 \times 10^5$ cm²/(V · s) (Fig. 4). However, this is an unstable state and the samples return to the state with *p*-type conductivity over a period of two days. Continuing illumination with the same power density produces a reduction in the hole concentration and, after a certain inverval of time, the crystals assume the n-type state throughout the temperature range that was investigated. The concentration of carriers with the characteristic temperature dependence is close to the electron concentration in *n*-type crystals in the original state (prior to illumination). After this transition, the crystal becomes stable and there are no changes in the electron concentration or their mobility as illumination continues with W = const. However, when the power density is stepped up to $W_3 = 40 \text{ V/cm}^2$, the concen-



FIG. 2. Integrated reflection intensity R_i of quasi-forbidden (222) reflection as a function of exposure time for InAs samples: *1*—excess In, 2—excess As.



FIG. 3. Carrier concentration as a function of exposure time for InAs samples with excess As at the following temperatures (in K): 1—300, 2—77. Power densities (W/cm²): W_1 =15, W_2 =25, W_3 =40, W_4 =4

tration at 77 K and at 300 K again increases, as it does in the case of crystals with initial *n*-type conductivity [Fig. 1, t=5.5 h and Fig. 3, t=9 (h)] but at higher values of W and



FIG. 4. Temperature dependence of electron mobility in InAs crystals: 1—calculated for the case of scattering by lattice vibrations.⁵ Crystal experiments: 2—initial crystal with excess of In, 3-5—excess of As. Measurements on *n*-type regions: 3—unstable, 4—stable, 5—simultaneous application of constant electric field and laser radiation.



FIG. 5. Temperature dependence of carrier concentration for InAs samples: I—InAs sample with excess of In after a 13-hour exposure, 2—InAs sample with excess As in a region with stable *n*-type conductivity prior to the simultaneous application of the electric field and laser radiation (9 h, 30 min), 3—InAs sample with excess As in a region with stable *n*-type conductivity under the simultaneous application of the electric field and laser radiation (the solid curve is theoretical).

longer exposure. The power density is then substantially reduced to $W_4=4$ W/cm², and a constant electric field E < 0.1 V/cm is applied to the sample parallel to the electric vector in the laser wave. It was shown in Ref. 6 that the laserstimulated changes in the lattice in this case occur much more rapidly and, moreover, a directed migration of intrinsic and impurity components occurs with increasing exposure to the simultaneous action of the fields. In InAs, the electron concentration begins to fall in the presence of these fields (Fig. 5).

The results of these experiments can be explained by assuming that the changes in the crystal are not thermal, but are related to the laser-stimulated tranformations in the set of intrinsic point defects.

As in other semiconducting compounds such as GaAs, PbSnTe, and PbSnSe (Refs. 6 and 7), the laser-stimulated transformations of InAs occur in both sub-lattices, but at different rates. The metal component usually reacts more actively to a change in the laser power density than to changes in the dose, which is in fact confirmed experimentally.

The same mechanism for laser transformation of defects is typical for samples with excess As. The particular form of the function $R_H(T)$ that is observed only when the electric field and the laser radiation are applied to InAs (Fig. 5) is unusual and may be connected with a resonance level in the conduction band that transfers electrons to this band when the temperature is reduced. By analyzing the form of $R_H(T)$ we were able to calculate the position of this hypothetical level on the assumption that the donor level was formed by the *s*-type wave functions:

$$E_d(T) = E_d(0) - \alpha T$$

where $E_d(0) = 0.057 \pm 0.005$ eV and $\alpha = (2.0 \pm 0.2) \times 10^{-4}$ eV/K. As already noted, when the crystals with excess As is illuminated by laser radiation, there is a characteristic region with *n*-type conductivity and an anomalously high mobility



FIG. 6. Relative volume fraction of distorted lattice as a function of exposure time for InAs samples with excess In.

(Fig. 4). This state is not observed in crystals with excess In. It is clear from Fig. 4 that the electron mobility in the original samples is not very high because the best InAs crystals, grown by the Czochralski method, had mobilities reaching $\mu_{77} = 5 \times 10^4$ cm/(V·s) at liquid-nitrogen temperatures. Naturally, the greater the concentration of clusters of intrinsic components or impurities, the lower the electron mobility.^{8,9} Figure 6 shows the relative volume fraction of lattice distortions as a function of the exposure time. It is clear that the quantity ρ_0 monotonically decreases with exposure time, indicating a reduction in the volume fraction of large-scale inhomogenities in the crystal. This result is in agreement with the measured stoichiometry (spreading of coagulated intrinsic components during exposure leads to a change in state of the atoms in the lattice) and also with the increase in carrier mobility with increasing dose of radiation. We note, however that this mechanism is hardly the dominant one in the unstable phase of *n*-type conductivity, where for relatively high volume fraction of distortions the mobility at T=77 K reaches values that are actually restricted by the theoretical limit for scattering by lattice vibrations under the illumination (Fig. 4, curve *I*). Interestingly, when $N_I \approx n_{77} = 2 \times 10^{16} \text{ cm}^{-3}$, the mobility should not exceed $\mu_{77} = 7.5 \times 10^4 \text{ cm}^2/(\text{V} \cdot \text{s})$ (when scattering by ionizing impurities and lattice vibrations is taken into account), where N_I is the concentration of ionized impurities. The measured mobility is higher than this value by an order of magnitude.

A possible reason for this behavior of $\mu(T)$ is the ordering of the set of charged scattering centers in the field of the laser radiation, due to Coulomb repulsion and the formation of corrrelated mixed-valence point defects.¹⁰ This ordering of scattering centers requires concentrations of not less than 5×10^{18} cm⁻³, which is feasible in compensated semiconductors with low point-defect formation energies, e.g., III-V compounds. We note again that this situation occurs only in the case of laser-stimulated inversion from *p*- to *n*-type conductivity, followed by a transition to the stable *n*-type.

The carrier mobility in crystals with stable n-type conductivity is somewhat lower than the mobility observed in samples with excess In after exposure to laser radiation. This suggests a higher concentration of scattering centers in samples with excess As.

Moreover, it is clear from Fig. 4 that, as the power density increases, the initial rise in the electron concentration is accompanied by a reduction in mobility. However, the character of the temperature dependence remains nearly the same. It is important to emphasize the change in the mobility $\mu(T)$ throughout the temperature range when the laser radiation with power density reduced by an order magnitude and weak electric field are applied together (Fig. 4, curve 5). In this case the mobility increases with temperature, then reaches a maximum, and finally falls. This shows that there is a change in the scattering mechanism not only at low temperatures T < 130 K, but also at higher temperatures 130<T<400 K. The function $\mu(T)$ is largely determined for T < 130 K by scattering by ionized impurities that are generated under the simultaneous application of the laser radiation and the external field. This contribution increases with increasing radiation dose, in good agreement with the dose dependence of the carrier concentration in the same interval. It follows from the analysis of $R_H(T)$ and the intensities of quasi-forbidden reflections that these centers probably include As atoms in the interstices of their planes.

4. CONCLUSION

We conclude that the effect of laser radiation, with $\hbar \omega < E_g$ and power density much less than the threshold

value necessary for thermal damage to the crystal, can be used to vary the electrical and structural properties of InAs as a result of the redistribution of electrically neutral intrinsic components in the field of the laser wave.

- ¹P. K. Kashkarov, V. I. Petrov, and D. V. Ptitsyn, Fiz. Tekh. Poluprovodn. **23**, 2080 (1989) [Sov. Phys. Semicond. **23**, 1287 (1989)].
- ²F. F. Sizov and S. V. Plyatsko, J. Cryst. Growth **92**, 571 (1988).
- ³I. Fujimoto, Jpn. J. Appl. Phys. 23, 287 (1984).
- ⁴V. V. Lider, F. N. Chukhovskii, and V. N. Rozhanskii, Fiz. Tekh. Poluprovodn. , **19**, 1231 (1977) [Sov. Phys. Semicond. **19**, 816 (1985)].
- ⁵D. L. Rode, Phys. Rev. B **3**, 3287 (1971).
- ⁶Yu. S. Gromovoj, S. V. Plyatsko, F. F. Sizov, and L. A. Korovina, J. Phys. Condens. Matter, 2 10391 (1990).
- ⁷V. P. Klad'ko and S. V. Plyatsko, Pis'ma Zh. Teor. Fiz. **22**, 32 (1975) [JETP Lett. **22**, 14 (1975)].
- ⁸A. N. Baranov, T. I. Voronina, A. A. Gorelenok, T. S. Lagunova, A. M. Litvak, M. A. Sipovskaya, S.£. Starosel'tseva, V. A. Tikhomirova, and V. V. Sherstnev, Fiz. Tekh. Poluprovodn. **26**, 1623 (1992) [*sic.*]
- ⁹ A. N. Baranov, T. I. Voronina, T. S. Lagunova, M. A. Sipovskaya, V. V. Sherstnev, and Yu. P. Yakovlev, Fiz. Tekh. Poluprovodn. 27, 421 (1993) [Semiconductors 27, 236 (1993)].
- ¹⁰ I. M. Tsidil'kovskii, Usp. Fiz. Nauk **162**, 63 (1992) [Sov. Phys. Usp. **162**, 85 (1992)].

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