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The Effect of Uncontrolled Impurities on Free Carrier Concentration in InAs After Thermal Treatment

S.K. Nikoghosyan[a], A.S. Hovhannisyan

A.I. Alikhanyan National Science Laboratory (Yerevan Physics Institute) Foundation, 2 Alikhanyan Brothers St., 0036, Yerevan, Armenia

[a] E-mail: nick@yerphi.am

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Abstract. In this work, the increase in the concentration of free electrons (*n*) in InAs after high-temperature heating followed by isochronous annealing is calculated under the assumption that uncontrolled impurities are present in the single crystals in the form of small complexes. It is shown that these complexes dissociate during annealing into individual impurity ions, which diffuse into the lattice and become donor centers (thermal donors), thereby causing an increase in *n*. The average dissociation energy of the impurity complexes, ΔW, was determined, and the dependence of the concentration *n* on the annealing time τ was calculated within the framework of a model of closely spaced ion pairs, using experimental data obtained at fixed annealing temperatures of 450 °C, 650 °C, and 850 °C. It was established that the value of ΔW depends on the impurity concentration, the diffusion coefficient of the impurity ions, the annealing temperature, and the dielectric constant of InAs. Comparison between the calculated and experimental curves of the additional electron concentration $\Delta n(\tau)$ showed that Δn increases monotonically with both annealing temperature and duration. At an annealing temperature of 450 °C, the calculated and experimental $\Delta n(\tau)$ curves exhibit nearly complete agreement. However, at higher annealing temperatures, certain discrepancies appear: for short annealing times ($\tau < 60$ h), the calculated $\Delta n(\tau)$ values lie below the experimental ones, whereas for $\tau > 60$ h, the opposite tendency is observed. Furthermore, this discrepancy decreases as the annealing temperature increases. Probable causes of the observed features are discussed and corresponding conclusions are drawn.

Keywords: Concentration of free charge carriers, InAs semiconductor single crystal, high-temperature heating, residual impurities, thermal donors, model of closely situated ion pairs

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1. Introduction

Binary monocrystalline InAs is a direct-bandgap semiconductor with a narrow band-gap and charge carriers with high mobility. These properties make it an ideal material for developing new types of heterojunctions, generating terahertz radiation, fabricating infrared windows, lasers, and sensitive magnetic-field detectors (Hall sensors) [1–3]. It is important to note that the application of InAs is limited by its initial purity. During device fabrication, InAs single crystals undergo complex thermal treatments that significantly change their physical characteristics, and understanding these processes is of great scientific and practical interest. It is known that prolonged high-temperature annealing followed by rapid cooling to room temperature increases the concentration of free electrons in InAs single crystals [4–6]. P-type samples can even convert to n-type [4, 5]. These effects are attributed to the presence of uncontrolled (residual) impurities—such as copper, sulfur, selenium, carbon, and tellurium—in the initial samples [1, 4–8]. The results obtained after thermal treatment also depend strongly on factors such as the degree of compensation, dislocation density, stoichiometric deviations, growth method, and thermal-processing conditions [4–6]. Earlier works suggested that in the initial state, uncontrolled impurities accumulate near dislocations and remain electrically inactive according to the Kurtz–Kulin model [4, 5]. Upon heating, these impurities are released from their bonds with dislocations and enter the lattice, where they act as donors (thermal donors), while rapid quenching "freezes" this state [4, 5]. Such impurities are present in all $A^{III}B^{V}$ compound semiconductors, and obtaining them in completely pure form remains technologically impossible [1–9]. In specially undoped InAs, InP, GaP, and related materials, the concentration of free carriers at room temperature typically reaches ~10^{16} cm^{-3} or higher, far exceeding the intrinsic level. Samples with lower carrier concentrations are usually heavily compensated [1–9]. The Kurtz–Kulin model also suggested a dependence of the number of thermally generated electrons on dislocation density [4, 5]. Later studies confirmed that changes in free-electron concentration after thermal treatment in InAs single crystals are indeed caused by the release of uncontrolled copper impurities from dislocations, with the rate of this process depending on dislocation density [6–8]. Within the range of initial dislocation densities from 10^3 to 10^5 cm^{-2}, samples with higher densities show the strongest change in electron concentration during annealing and subsequent aging [6]. Moreover, the increase in free-carrier concentration is maximal in samples with a high degree of compensation, i.e., lower mobility and higher initial impurity content [4–7]. This correlates with our earlier results demonstrating a slight decrease in thermal conductivity near liquid-nitrogen temperatures after irradiation of InAs with high-energy electrons (50 MeV) [10]. This indicates that numerous impurity centers already exist in the lattice and strongly scatter phonons even prior to irradiation, so thermal conductivity changes only slightly afterwards. Nevertheless, the existing body of research still lacks a definitive theoretical mechanism explaining the increase in free-carrier concentration [11–13]. One reason may be that, as in silicon, thermal donors of different chemical nature and similar behavior are generated in InAs [14]. Additionally, the variety of defect complexes in InAs is broader than in silicon, complicating their detection and study [2].

In this work, using available and our own experimental data, we propose that the increase in free-electron concentration after high-temperature treatment is caused by the presence of uncontrolled impurities in the form of simple complexes.

2. Theoretical and experimental approaches

To analyze the increase in the concentration of free electrons in InAs after prolonged high-temperature annealing followed by rapid quenching, we use the data from [4, 5] as a representative example. Figure 1 shows the experimental dependence of the additional electron concentration Δn on heating time τ in the range 0–100 hours for annealing temperatures of 450 °C, 650 °C, and 850 °C, followed by quenching of n-InAs samples [4, 5]. For comparison, our calculated $\Delta n(\tau)$ curves are also provided. To calculate Δn, we chose a model complex consisting of closely spaced ion pairs such as $Cu^{+}O^{-}$ and $Cu^{+}S^{-}$, etc. To calculate Δn, we consider a model in which uncontrolled impurities form tightly bound ion-pair complexes, such as $Cu^{+}O^{-}$, $Cu^{+}S^{-}$, and similar pairs. For convenience, we analyze the reverse process—i.e., the association of two free ions into a bound complex—represented schematically as:

$$\mathrm{Cu^{+} + S^{-} \rightleftarrows Cu^{+}S^{-}} \qquad (1)$$

When copper and sulfur ions are widely separated, they may not remain ionized; however, the binding process can still be described kinetically. The characteristic relaxation time of ion-pair formation is given by

$$1/K = \tau, \qquad (2)$$

where K is the reaction-rate constant for reaction (1). Assuming the concentrations of both ions are equal, each positive ion eventually pairs with its nearest negative neighbor. The capture rate can then be expressed [15] as:

$$- dN_F/dt = 4\pi N^2 \cdot R \cdot D = K \cdot N_F\,, \qquad (3)$$

where N_F is the concentration of free or unbound ions, N is the initial concentration of ions, R is the capture radius—i.e., the distance within which two ions bind—and D is the diffusion coefficient of the more mobile ion. Following [15], the capture radius is approximated as $R=q^2/\varepsilon kT$. Substituting this into Eq. (3), we obtain the characteristic relaxation time:

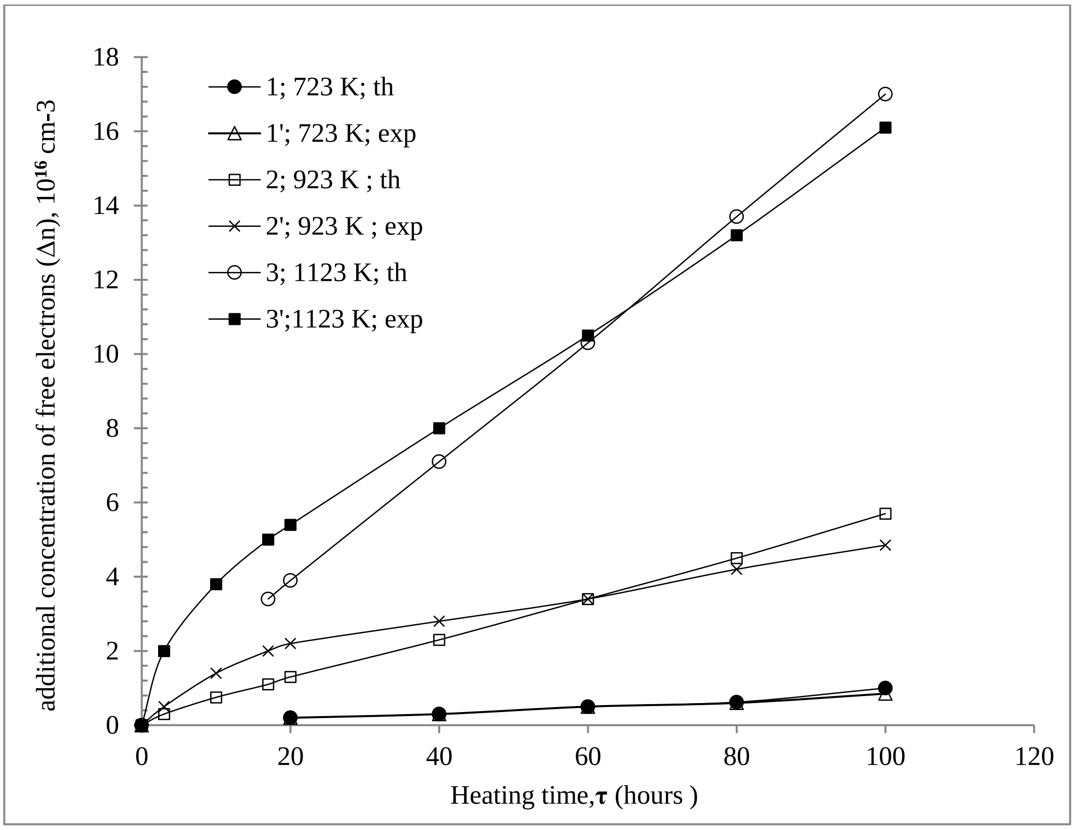

Fig. 1. Dependence of the additional increase in free-electron concentration Δn in n-InAs on the heating time τ at temperatures of 723 K (450 °C), 923 K (650 °C), and 1123 K (850 °C), followed by rapid quenching to room temperature. The carrier concentrations were determined from Hall-effect measurements at room temperature. The curves without primes show the results of our theoretical calculations (th), and the curves with primes correspond to the experimental results (exp) reported in [4].

$$\tau = \varepsilon kT/4\pi\, q^2 \cdot N \cdot D, \qquad (4)$$

where ε is the dielectric permittivity, k is the Boltzmann constant, and q is the ionic charge. Equation (4) allows us to determine the diffusion coefficient D of the mobile impurity ion, provided τ, N and T are known. According to [15, 16], the temperature dependence of D can be written as:

$$D = D_0 \cdot \exp(-\Delta W/kT), \qquad (5)$$

where D_0 is a pre-exponential factor and ΔW is the activation energy for diffusion (in this context, the dissociation energy of the impurity complex).

3. Results and discussion

Using the data from [4, 5] and determining N by extrapolating to $\sim 1.7\cdot 10^{17}$ cm^{-3}, we calculated the diffusion coefficient D of the mobile ion for several annealing temperatures: T_1 = 723 K, T_2 = 923 K, and T_3 = 1123 K. Substituting these values into Eq. (5), and assuming D_0 is temperature-independent, we obtain an average dissociation energy of the complexes, $\Delta W \approx 0.53$ eV. This value enables a self-consistent calculation of the additional concentration of free electrons, Δn, for any heating duration τ. Physically, ΔW represents the depth of the potential well that confines the ion. To escape, the ion must acquire energy equal to ΔW. At moderate temperatures, the average thermal energy of a lattice atom is on the order 0.1 eV; overcoming the barrier thus requires a rare thermal fluctuation of magnitude ΔW. During thermal vibrations, an atom attempts to overcome the potential barrier roughly once per second. Most attempts fail because the energy is insufficient, but on rare occasions a fluctuation provides the required energy ΔW, enabling the ion to escape. The frequency of such escape events is given by

$$f_m = \mathbf{z}\cdot \nu \cdot exp(-\Delta W/kT), \qquad (6)$$

where z is the number of nearest interstitial lattice sites. For a face-centered cubic (FCC) lattice, z = 12; ν is the Debye frequency equals to approximately 10^{13} s^{-1}. To convert the hopping frequency into the concentration of additional carriers, we assume that each ion or atom that crosses the barrier donates one electron to the conduction band. Furthermore, formula (6) must be multiplied by the heating time τ, the concentration of complexes N, the probability of forming an energy fluctuation of magnitude, ΔW, and the probability that such a fluctuation occurs specifically in a complex. The exact forms of these probabilities are not known to us, so we represent Δn in the following form:

$$\Delta n = c\cdot f_m\cdot \tau \qquad (7)$$

Here, c is a fitting parameter, which we determined by matching Δn to the experimental results presented in Ref. 4 at a heating temperature of T=723K. For c, we obtained a value of approximately 1. Thus, for Δn we finally obtained:

$$\Delta n = \mathbf{z}\cdot \nu \cdot \tau \cdot \exp(-\Delta W/kT) = 1.2\cdot 10^{14}\cdot \tau \cdot \exp(-0.53/kT). \qquad (7')$$

It is important to note that the activation energy calculated by us ΔW= 0.53 eV almost coincides with the value of 0.52 eV obtained in [8], which is responsible for the growth of free carriers in InAs, and is also associated with contaminating copper atoms (Cu) penetrating there from the melt during the growth process and from the quartz ampoule during high-temperature annealing [4-7]. According to work [8], after heat treatment, Cu impurities leave their electrically passive (interstitial) positions and, entering the spatial lattice of the n-InAs single crystal, become additional donor centers. However, the activation energy ΔW=0.23 eV obtained in [6] for InAs is greatly underestimated compared to the above values, and the probable reason for such a discrepancy may be the lack of consideration of Cu diffusion in quartz (ampoules) and the surface barrier during annealing. It should be noted that the values of ΔW in the elementary semiconductor Si and in the semiconductor compounds GaAs, GaSb and InSb are also very close. Moreover, in the semiconductors Si, GaAs and GaSb, the same activation energy is observed ΔW=0.53 eV [16]. The found value ΔW = 0.57 eV in InSb is due to the activation of interstitial impurity atoms Te [16]. Additionally, it is noted that in InAs crystals irradiated by electrons with energies of 3 MeV and 2 MeV after high-temperature heat treatment, the values of 0.6 eV [11] and 0.53 eV [13] were obtained for ΔW, respectively. It is assumed that the centers responsible for these energies in InAs are small complexes that include uncontrolled (residual) impurities and intrinsic defects (such as V_{As}, V_{In}, As_{In} and In_{As}) [11-13]. The found value of ΔW = 0.57 eV in InSb is attributed to the activation of interstitial impurity atoms of Te [16]. Additionally, it is noted that in InAs crystals irradiated by electrons with energies of 3 MeV and 2 MeV, the values of of 0.6 eV [11] and 0.53 eV [13] were obtained for ΔW, respectively. It is assumed that the centers responsible for these energy levels in InAs are small complexes that include uncontrolled (residual) impurities and intrinsic defects (such as V_{As}, V_{In}, As_{In} and In_{As}) [11-13].

Figure 1 also shows that, at a fixed heat treatment temperature, the experimental and calculated $\Delta n(\tau)$ curves increase monotonically with increasing τ. Moreover, a significant slowdown in this increase is observed in the region above 20 hours. It is noteworthy that in work [6], when heating starting from 500˚C and above, with a heating time τ greater than 20 hours, the $\Delta n(\tau)$ curves exhibit saturation, and the observed maximum increase in Δn with rising heating temperature increases sharply. It is evident that the experimental and theoretical $\Delta n(\tau)$ curves we obtained at a heat treatment temperature of 450˚C coincide (Fig. 1). However, at higher heat treatment temperatures, an increase in the growth rate Δn is observed as function of the heating time τ, but saturation does not occur. Moreover, if the experimental curves of the $\Delta n(\tau)$ dependence in the region $\tau < 60$ h are positioned above the theoretical ones, then for $\tau > 60$ h the opposite behavior is observed. This behavior is likely due to the fact that heat treatment causes both the decomposition of the original complexes formed by uncontrolled impurities and the formation of new complexes involving newly created structural defects and the original impurities (both uncontrolled and intentionally introduced). The formation of these complexes can explain the observed effect of decreasing the growth rate Δn in InAs, which is stimulated by increases in temperature and time during the heat treatment of the single crystal [6]. Further research is required to definitively elucidate the causes of this behavior, particularly concerning the absence of the Δn saturation effect.

4. Conclusions

Thus, the experimentally observed increase in the concentration of free charge current carriers in InAs single crystals after long-term high-temperature annealing can be attributed to the presence of small complexes formed by uncontrolled impurities. To characterize these complexes, the average dissociation energy, $\Delta W = 0.53$ eV, was determined. It was found that for silicon and the $A^{III}B^{V}$ semiconductor crystals GaAs, GaSb, InSb, and InAs, the ΔW values are very similar, ranging from 0.52 to 0.60 eV. Using this energy value, theoretical time dependences of the additional increase in free electron concentration, $\Delta n(\tau)$, during heat treatment were calculated and compared with the corresponding experimental data. The $\Delta n(\tau)$ curves exhibit an increasing trend with increasing annealing time τ, and the growth rate increases as the processing temperature rises. However, at a fixed temperature for long heating times ($\tau > 20$ h), a pronounced slowdown in the growth of $\Delta n(\tau)$ is observed. In contrast, [6] reports a saturation behavior in this region. The best agreement between theory and experiment was observed at a processing temperature of 450 °C, whereas at higher temperatures and longer times τ the curves display distinct characteristic features. It was established that with increasing temperature, the relative difference between the experimental and theoretical curves in both regions decreases. We hypothesize that these features may be due to the formation of new complexes involving the original impurities and thermally generated intrinsic defects, which would reduce the concentration of thermal donors. Further research is required to fully elucidate the mechanisms responsible for the absence of a saturation effect in Δn.

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