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# **Charge State Of Impurity Atoms In Semiconductors Studyed By The Emission Mössbauer Spectroscopy Method**

**Ergash Yuldashevich Turaev**

**Doctor Of Physical And Mathematical Sciences, Professor Of Termez State University, Uzbekistan**

**Jasurbek Jumaev Master's Students Of Termez State University, Uzbekistan**

**Shahlo Karimova Master's Students Of Termez State University, Uzbekistan**

#### **ABSTRACT**

When studying the charge state and symmetry of the local environment of impurities, based on the data of nuclear gamma-resonance spectroscopy, it is concluded that the state of impurity atoms depends both on the type of conductivity and on whether these atoms are in the surface layer or in the bulk of semiconductors.

## **KEYWORDS**

Charge state, symmetry, local environment of impurities, nuclear gamma-resonance spectroscopy, semiconductor, surface layer, atoms

## **INTRODUCTION**

A number of works are devoted to the study of the properties of semiconductor compounds doped with iron . It has been shown, in particular, that the introduction of iron into GaAs leads to the appearance in the forbidden band of two deep-lying levels Eo +0.37 and Ev

+ 0.52 eV; however, until now it has not been clarified to which the indicated levels correspond to isolated iron atoms or the same complexes of the "impurity-impurity" type. It should also be noted that the concentration distribution of iron in GaAs after diffusion is

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characterized by two regions - near-surface

## **MATERIALS AND METHODS**

and bulk].

The complex concentration distribution, apparently, is caused by the different state of the impurity in the surface and bulk regions of the crystal. In the bulk of GaAs, Fe atoms are in a cubic environment and can be regarded as isolated. The levels found in the band gap of iron-doped gallium arsenide can be attributed to these isolated atoms. In the near-surface layer, iron atoms form complexes with vacancies, and it can be assumed that such complexes should correspond to special levels in the forbidden band of GaAs.

For iron atoms located both in the bulk and in the near-surface layer of GaAs, a charge exchange process was observed depending on the position of the Fermi level. Since the parameters of the NGR spectra depend on the electronic structure and the symmetry of the arrangement of impurity atoms in the crystal, it was of interest to study the state of iron atoms in GaAs by the Mössbauer method. The use of the emission version of spectroscopy made it possible to obtain information on impurity atoms both in the bulk of the sample and in its near-surface layer.

#### **1. Experimental technique**.

As a starting material, we used p and n-type GaAs samples doped during growth with zinc  $(p = 1.6 - 1018$  cm-3) and tellurium  $(n = 1.6 - 1018)$ cm-3). Samples in the form of plates were cut from single-crystal ingots oriented in the <111> direction. The solubility of iron in GaAs is low ( $\sim$ 1017 at-cm-3 at 1050  $^{\circ}$  C [4]), and therefore the emission version of spectroscopy was used to record the Mössbauer spectra - the 57Co

isotope was introduced into the samples under study, after the decay of which the Mössbauer level 57mFe. Obviously, the information of emission Mössbauer spectroscopy refers to cobalt, when we mean the location of atoms in the lattice, the possibility of its complexation with lattice defects; and at the same time, this information refers to iron when it comes to the charge state of impurity atoms.

In our experiments, 57Co was electrolytically deposited on the surface of the samples, which were then subjected to diffusion annealing in evacuated quartz ampoules at 1050 ° C for 25 h. To reduce the evaporation of arsenic from gallium arsenide, a GaAs powder was placed in the ampoules, providing an equilibrium value of vapor pressure arsenic over the sample due to its evaporation from the powder. NGR spectra were recorded on an electrodynamic setup at 295°K with an absorber K4Fe (CN) 6 • ЗН20. The spectra were recorded twice before and after removal of the surface layer ( $\sim$ 150 µm thick).

#### **2. Experimental results and their discussion**

As already indicated, the concentration distribution of cobalt and iron in GaAs is characterized by two regions - near-surface and bulk. The concentration curves are characterized by an increase in the concentration of cobalt in the near-surface region [3]. In this case, it can be assumed that in the near-surface region enriched with nonequilibrium vacancies diffusing from the surface, cobalt interacts with them. In the bulk of the crystal, where the concentration of such nonequilibrium vacancies is low, the interaction of cobalt with them can be neglected.

57Со (57Fе) NGR spectra for atoms in the surface layer  $($   $\sim$  20  $\mu$ ) depend on the type of conductivity of the original samples. For n-type samples they were singlet, somewhat broadened lines, and for p-type samples quadrupole doublet. The results of processing the experimental spectra are shown in the table. Note that the NGR spectra for atoms in the GaAs subsurface layer are close in their parameters to the spectra given in  $[5]$ .

Isomeric shift δ (relative to metallic iron, mm / sec.) And quadrupole splitting ΔЕQ (mm / sec.) Of the NGR spectra of impurity iron atoms in gallium arsenide (at 295о K).



After removing from the surface of a layer with a thickness of 150 microns, the NGR spectra changed - they were singlet lines in both n- and p-type samples, but the isomeric shifts were different (see table). Thus, it can be concluded that the state of impurity iron (cobalt) atoms in GaAs depends both on the type of conductivity of the samples and on whether these atoms are in the surface layer or in the bulk of the sample. Charge state and symmetry of the local environment of iron (cobalt) atoms in the bulk of GaAs. After diffusion doping with cobalt of p-type GaAs samples, they retained the hole conductivity, while the hole concentration slightly increased. As a result of the diffusion of cobalt, the initial n-type samples also did not change the sign of the current carriers.

As already mentioned, the Mössbauer spectra from bulk impurity atoms in n- and p-type

samples were singlet lines differing only in the isomeric shift. Apparently, in both cases, the impurity atoms are in a cubic environment, and the difference in isomeric shifts is explained by the difference in the charge state of iron.

The values of the isomeric shifts of the spectra 〖MGR〗 ^ 57m Fe in p-type samples are less than in n-type samples, which corresponds to a decrease in the electron density on 57Fe nuclei on going from p-type samples to n-type samples.

This fact can be explained by the fact that a hole in p-type samples populates the 3d-shell of an iron atom and thereby decreases the screening by 3d electrons of internal selectrons, i.e., the transition from p-type samples to n-type samples leads to a change in the electron configurations of impurity iron atoms from  $\left[\begin{smallmatrix} 3d \end{smallmatrix}\right]$  ^ 5 to  $\left[\begin{smallmatrix} 3d \end{smallmatrix}\right]$  ^ 6 (the process of charge exchange of impurity iron atoms depending on the position of the Fermi level).



Fig. 1. Mössbauer spectra of 57Co 57mFe in the volume of GaAs.

α-sample of n-type, b-sample of p-type.

Absorber K  $4 \times (FN)$ ]  $6 \cdot 3H$  2 O. T = 295 ° K.

## **CONCLUSION**

Note that in the study of the state of impurity iron atoms in GaAs by the EPR method [5], the spectra were obtained only for p-type samples. The absence of EPR spectra for n-type samples indicates a charge exchange of impurity iron atoms upon going from p-type samples to ntype samples. In p-type samples, the EPR spectrum corresponds to  $\left[\begin{matrix}Fe\end{matrix}\right]$  ^ (3+) ions with the electronic configuration  $\left[3d\right] \wedge$  5 (^

6 S), while in n-type samples the EPR spectra disappear due to ionization of impurity centers with the formation of an electron configuration  $\[ \&3d \]$  ^ 6 (^ 5 D), which does not give in the field of tetrahedral symmetry of the EPR spectrum. Thus, there is complete agreement between the results of NGR and EPR spectroscopy.

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