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Solubility, diffusion and electrical activity of Na in bulk Ge crystals

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ABSTRACT

By studying the drift of Na^+ ions in the firstly grown Na-doped bulk Ge crystals as well as by analyzing optical and some other characteristics of this material, the following conclusions are made, many of which are different from the commonly accepted statements: (1) Ge can be uniformly doped with Na during the bulk Ge crystals growth from the melt; (2) maximum solubility at room temperature and distribution coefficient of Na in Ge are $(0.3–1)\times10^{15}$ cm^{-3} and $(0.7–2.3)\times10^{-7}$, respectively; (3) Na is a donor impurity in bulk Ge, and Na atoms introduced during the crystal growth are predominantly electrically active; (4) the evaluated values of diffusion parameters of Na in Ge are as follows: the diffusion coefficient $D=3.6\times10^{-7}$ cm^2/s, pre-exponential factor $D_0=0.13$ cm^2/s, the activation energy for diffusion $Q=0.33$ eV; (5) Na is an interstitial impurity in Ge and rather rapidly drifts in an electric field, most likely, via interstitial sites; (6) the resistance distribution along the crystal length may be changed by DC electric field application and remain stable at the long-term crystal storage. The stability in the Ge:Na properties opens the possibility for using Ge:Na crystals not only for creating passive optical elements of infrared imaging technique, as we are doing now, but also for the electrical appliances, in particular for the substitution of the thermally unstable Li for Na in germanium detectors of γ-radiation.

1. Introduction

Actively discussed at present, the prospects for creation the Ge-based modern high-speed nanoelectronic devices are limited, among other things, by the fact that during the years of Si dominance in electronics, many studies of Ge were not sufficiently intensive. In particular, stability and mechanisms of diffusion of many impurities in Ge remain unknown and, as a result, it is difficult to control the properties of Ge-based devices which contain these impurities [1].

For many years Na as an impurity in Ge has been considered promising to replace Li, unstable even at room temperature, in Ge detectors of γ-radiation [2]. In addition, at present Na serves as a main impurity in optical-grade Ge crystals successfully used for manufacturing optical elements of infrared technique with improved parameters [3,4]. However, Na remains to be one of the least studied impurities as compared with many other impurities in Ge. The tables of physical parameters of different impurities in Ge, published in the reference books, monographs and reviews, either do not include any Na parameters or those parameters differ by up to several orders of magnitude. For example, the published values of Na maximum solubility in Ge measured at close temperatures, differ by more than two orders of magnitude – from $8\cdot10^{15}$ cm^{-3} at T=610 °C to $1\cdot10^{18}$ cm^{-3} at T=750 °C [5]. In other scientific works the absence of the mutual solubility of Ge and alkaline metals in the solid state was claimed [6]. On the basis of some experiments the possibility of Na diffusion into Ge was not denied, and the conclusions about the vacancy mechanism of diffusion and an acceptor nature of Na in Ge were made [7].

The results on the electrical activity of Na in Ge are also contradictory. For example, many years ago a conclusion was drawn [8] that the energy levels of alkali metal impurities (other than lithium) cannot be located near the edges of c- and v-bands. It was shown later [9] that although radioactive ^{24}Na isotopes diffused into p-Ge wafers with heating, any n-type surface layers were not then detected by the thermoelectric measurements. This effect was explained by the fact that interstitial Na_i^+ ions form neutral associations by interacting with the negatively charged Ge vacancies or acceptor impurities. The conclusion about the absence of Na electrical activity was also made on the basis of studies of vapor diffusion of radioactive Na isotopes into Ge [10]. However, relatively recent studies of Na implantation into p-Ge have revealed, via thermoelectric measurements, the donor behavior of this impurity although donor properties exhibited only a few tenths of a percent of the total number of implanted Na ions [2]. A similar quantitative effect was previously observed in silicon, wherein the concentration of donors in the layer formed by Na diffusion, was three orders of magnitude lower than the total content of this impurity [11].

As regards the general concept of shallow impurities in Ge, it was summarized as follows [12]: “Most of the shallow impurity states in Ge

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Table 1
Concentrations of impurities in Ge:Na crystals (with a free electrons density about 10^{14} cm^{-3}) measured by glow discharge mass spectrometry (line 2) and by neutron activation analysis (line 3).

1	Impurity	Li	Na	K	Sb	P	As
2	Concentration, cm^{-3}	$< 4.4\times10^{12}$	3.4×10^{14}	2.7×10^{13}	1.3×10^{12}	2.0×10^{12}	5.9×10^{12}
3	Concentration, cm^{-3}		9.7×10^{14}		3.5×10^{11}		

are formed by substitutional impurity atoms. Impurity atoms or ions must be very small to occupy an interstitial state. Appreciable numbers of interstitials have been demonstrated only for atomic H and He, and for Li^{+} ions. The remaining impurities take up substitutional sites and diffuse into the lattice by exchanging lattice sites with vacancies".

However, the assumption that Na in Ge cannot be electrically active and cannot occupy interstitial sites, in our opinion, is not confirmed. This is evidenced, in addition to the above-mentioned results on Na implantation in Ge [2], by the results of our previous work [3]. We had managed to grow from the melt the large Ge crystals uniformly doped with Na and to prove that their optical and other characteristic are typical of the optical-grade germanium which, as it is known [13,14], must contain a shallow donor impurity at a density from 5×10^{13} cm^{-3} to 4×10^{14} cm^{-3}. Moreover, since some optical characteristics of the Na-doped germanium proved to be even better than those of conventional optical-grade Ge doped with substitutional V-group impurities (such as Sb), the large Ge:Na crystals, in a total amount of more than 2000 kg grown in our laboratory, have been successfully used for nearly two decades by some US, European and Ukrainian companies as a material for manufacturing lenses, screens and other passive elements of infrared imaging technique. It confirms that Na in Ge is not some "exotic" and uncontrollable contamination, but quite stable donor impurity suitable for a practical use.

Let us return to the second possibility for practical use of Na impurity in Ge, that is the creation of Na-doped Ge detectors of γ-radiation, similar to those doped with Li. Lithium is used in Ge detectors to compensate the charge carriers in the depletion region of p-Ge, but has the disadvantage that rapidly diffuses in Ge even at room temperature, whereupon the detectors must be stored at liquid nitrogen temperature. Hopes to use Na instead of Li were based on the fact that since the sodium ion radius larger than that of lithium, the diffusion of Na in Ge lattice at ambient temperatures may be slower than that of Li. In order to clarify the prospects for replacing Li to Na in these detectors, it is necessary to establish exactly the hitherto unknown values of some important parameters of Na impurity, such as maximum solubility of Na in solid Ge, the diffusion coefficient of Na in Ge crystals at room temperature and, most importantly, the associated degree of stability of the electrical characteristics of Ge:Na crystals with various Na distribution over the crystal volume, particularly during long-term crystal storage. All these issues are studied in the present work.

2. Experimental results

2.1. Solubility and distribution coefficient of Na in Ge

Solubility of Na in Ge crystals was evaluated on the basis of the results obtained by studying the large Ge crystals doped with Na during their growth from the melt by Stepanov method or by horizontal directional crystallization. As a source material, the zone-refined polycrystalline germanium of 9N grade purity was used. A distinctive feature of the doping process was that Na was introduced from the "unlimited" source and the amount of the introduced Na was not controlled. This significantly distinguishes the process of Ge doping with Na from the conventional process of Ge doping with V group elements, such as Sb, which is introduced in a predetermined amount by adding, to the Ge melt, the GeSb pellets containing a known quantity of Sb. The content of Sb introduced into the source germanium must be strictly controlled at a level from 5×10^{13} to 4×10^{14} cm^{-3} that is optimal for optical germanium. Otherwise, on the basis of the facts that the maximum solubility of Sb in Ge crystals (1.2×10^{19} atoms/cm^{3} [15]) significantly exceeds this level and Sb solubility in Ge has a retrograde character, the excess antimony may form inclusions while cooling Ge crystals from the growth temperature to room temperature, which inclusions result in increasing the optical scattering of infrared radiation passing through the Ge:Sb crystal [16].

We had developed a regime for Ge doping with Na, which made it possible to obtain Ge crystals with donor densities optimal for the optical-grade material. These densities correspond to Ge crystal resistivity between 10 and 25 Ω cm. We have found that such crystals have the best optical parameters, although, generally speaking, Ge crystals with a resistivity of 5–40 Ω cm in more or less degree are transparent for infrared radiation in the wavelength range from 1.8 to 18 μm [13].

While doping germanium raw material from the "unlimited" source of Na, in many years of our practice we have encountered with cases where the grown crystals had a resistivity above 40 Ω cm, i.e., they were close to Ge with the intrinsic conductivity whose resistivity equals to 47 Ω cm [17]. These failures we explained by random deviations of doping regime from the optimum one. However, never was the case when the resistivity of the grown crystals was below 5 Ω cm, which, according to [14], corresponds to the density of free electrons above 3×10^{14} cm^{-3}.

Table 1 shows the impurity concentrations in Ge:Na crystals, measured by glow discharge mass spectrometry (line 1) and neutron activation analysis (line 2). The measurements shown in line 1 were made in the Electrodynamics Laboratory "Proton-21" (Kiev, Ukraine) by means of the glow discharge mass-spectrometer Finnigan ELEMENT GD (Thermo Electron Corporation, Germany). The measurements which results are shown in line 2, were performed in the Institute for Nuclear Research, National Academy of Sciences of Ukraine, Kiev, by the comparative method of instrumental neutron activation analysis using the WWR-M nuclear research reactor. The resistivity of the crystals investigated was about 15 Ω cm, i.e., the density of free electrons in the crystals was about 1×10^{14} cm^{-3} [14]. As seen from Table 1, the density of free electrons and the Na content in the crystals are the same within one order of magnitude, although the Na content is slightly higher than the density of free electrons. This can be due, most likely, to formation of neutral complexes of Na ions with the negatively charged ions or vacancies, or to minor retrograde Na solubility. The solubility of such a nature is typical of many impurities in germanium [18]. In the case of crystal doping with such impurities, during cooling the crystal from the growth temperature to room temperature, the Ge-impurity solid solution becomes supersaturated and the excess impurity atoms would form the second phase and, hence, would become electrically inactive. But we have an argument against the hypothesis of Na second phase formation, at least, against the formation of micron-sized inclusions. Really, as evidenced by the results of our optical measurements [3], infrared radiation scattering in Ge:Na crystals is usually lower than that typical of Ge:Sb crystals, in which, due to retrograde Sb solubility, second-phase inclusions of character sizes about 6–9 μm may be formed, which scatter the infrared radiation [16]. Thus, examining the results shown in Table 1, it may be supposed that the retrograde solubility of Na in Ge, if any, is not essential.