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Development of epoxy composite protective coatings for increasing the radiation stability of n-Ge single crystals

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On the basis of Hall effect measurements, the temperature dependences of electrical conductivity and Hall constant were obtained for irradiated electrons with energy of 10 MeV and the flow of electrons $\Omega = 5 \cdot 10^{15}$ el/cm^2 of n-Ge single crystals coated with a layer of epoxy resin ED-20 with hardener PEPA (12 parts by weight), without and with fillers of iron or aluminum powders (30 parts by weight). From the analysis of the experimental results and theoretical calculations, it follows that the presence of such a coating layer increases the radiation resistance of germanium single crystals. It has been found that the best shielding ability from electron irradiation is provided by a layer of epoxy resin with a powder of iron. The obtained epoxy composite coatings can be used for germanium based semiconductor electronics as protective elements from the aggressive effects of radiation fields.

Keywords: Hall effect, epoxy resin, germanium single crystals, electronic irradiation, radiation defects.

На основе измерений эффекта Холла получено температурные зависимости электропроводности и постоянной Холла для облученных электронами с энергией 10 МэВ и потоком $\Phi = 5 \cdot 10^{15}$ эл./см^2 монокристаллов n-Ge, покрытых слоем эпоксидно-диановой смолы марки ЭД-20 с отвердителем ПЕПА (12 мас.ч.), как без наполнителя, так и с наполнителями порошков железа или алюминия (30 мас. ч). Показано, что наличие такого слоя покрытия повышает радиационную стойкость монокристаллов германия. Установлено, что лучшую экранирующую способность от электронного облучения имеет слой эпоксидиановой смолы с наполнителем порошка железа. Полученные епоксикомпозитные покрытия могут быть использованы для защиты элементов полупроводниковой электроники, изготовленных на основе германия, от агрессивного воздействия радиационных полей.

Розробка епоксикомпозитних захисних покриттів для підвищення радіаційної стійкості монокристалічного германію. *Ю.А.Удовицька, В.Т.Маслюк.*

На основі вимірювань ефекту Холла одержано температурні залежності електропровідності та сталої Холла для опромінених електронами з енергією 10 МеВ та потоком $\Phi = 5 \cdot 10^{15}$ ел./см^2 монокристалів n-Ge, покритих шаром епоксидно-діанової смоли марки ЕД–20 з твердником ПЕПА (12 мас.ч.), як без наповнювача, так і з наповнювачами порошків заліза або алюмінію (30 мас. ч). Показано, що наявність такого шару покриття підвищує радіаційну стійкість монокристалів германію. Встановлено, що найкращу екрануючу здатність від електронного опромінення має шар епоксидіанової смоли з наповнювачем порошку заліза. Одержані епоксикомпозитні покриття можуть бути використані для захисту елементів напівпровідникової електроніки, виготовлених на основі германію, від агресивного впливу радіаційних полів.

1. Introduction

At present, the task of ensuring high operational reliability indices of instruments and equipment in conditions of radiation exposure (electrons, protons, heavy charged particles, X-rays and gamma radiation) is quite acute. [1–5]. The radiation resistance of the equipment determines the term of its active use and failure-free operation. This is especially true for radioelectronic systems, which are part of the on-board equipment of spacecraft [3, 6]. Widespread use of semiconductor devices and integrated circuits sensitive to the action of ionizing radiation of outer space in the radio electronic equipment of the spacecraft, as well as the prolongation of the life of the spacecraft objects requires the provision of radiation stability for microelectronics' elements in a given radiation situation [2, 7]. One of the promising directions for the development of radiation-resistant apparatus is the application of local defense methods; in particular, the creation of special corps and coatings with integrated radiation protection screens [5]. These technologies allow the use of crystals of commercial and industrial chips instead of radiation-resistant chips, which makes it possible to reduce the cost of on-board equipment and expand the range of components used. In this regard, it is practical and commercially advantageous to create protective screens, coatings, or membranes made of polymer-composite materials that are more technological, light and cheap compared to metal enclosures. This requires detailed research on the effects of radiation exposure on the screening ability of such materials, especially when irradiated by high-energy particles.

So, the purpose of this work is to study the ability of epoxy polymers with various metal fillers to screen the affects of high-energy electron radiation.

2. Methodology and technique of experimental research

The first step in the preparation of the samples for investigating the ability of epoxy polymers with different metal fillers to screen the affects of high-energy electron irradiation was the production of germanium single crystals of required sizes and shapes for Hall effect measurements. The n-Ge single crystals were doped with Sb in concentration of $5{\cdot}10^{14}$ cm^{-3}.

For obtaining the shape of a rectangular parallelepiped, the germanium samples were carved using a machine tool, then polished with powders, and eventually treated with White's etchant. Before applying the contacts, the treated surface was washed with ethyl alcohol. The prepared n-Ge samples were equipped with contacts of pure tin with Sb admixture using a needle-tip soldering iron. Conductors 1–4 were tied up to the tin contacts. Voltage was applied to the contacts 1 and 2, and the Hall voltage was measured at the contacts 3 and 4. Before the contacts were attached, the treated surface was washed with ethyl alcohol. The contacts after attaching met the following requirements: 1) the contact resistance should be the same with two opposite directions of current; 2) contact resistance should not depend on the value of current; 3) the contacts must be mechanically strong, reliable and stable over time.

The next step was to apply epoxy polymer to germanium specimens. To do this, a germanium specimen in the harvested form was inserted into the cardboard box of the parallelepiped shape. Small openings were made in the cardboard box for the output of conductors 1–4. Then an epoxy polymer was poured to the box, till the germanium specimen was covered.

The epoxy polymer layer consisted of dianic resin (ED-20) with PEPA (12 parts by mass) (without fillers) and fillers of iron and aluminum powders (30 parts by mass). The process of curing the dianic resin lasted for 24 h under normal conditions. Additional heat treatment was carried out in a furnace at temperatures of 70 to 130°C. After the heat treatment, the samples were irradiated by accelerated electrons with an energy of 10 MeV and a flow $\Omega = 5{\cdot}10^{15}$ el./cm^2 on the microtron M-30 at the Institute of Electron Physics. The control of the irradiation temperature was carried out with the help of the copper-constantan thermocouple; its parameters were established to be stable to long action of the radiation. During the irradiation, the temperature variation did not exceed ±2 K and was regulated by blowing liquid nitrogen. To measure the electrical conductivity and electron concentration in unirradiated and irradiated n-Ge samples coated with a polymeric composite layer, a Hall effect technique was used. The sample under investigation was fixed to a special polygon and placed between the poles of the electromagnet perpendicular to magnetic field lines. The mag-

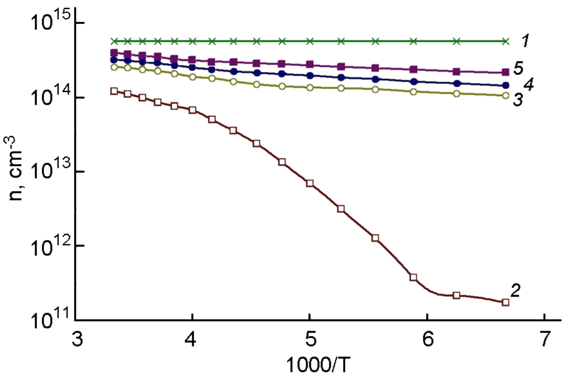

Fig. 1. Concentration vs temperature dependences of generated radiation defects in n-Ge specimens coated with a layer of epoxy composite: *1* — unirradiated n-Ge; *2* — irradiated n-Ge; *3* — irradiated n-Ge with a polymer layer; *4* — irradiated n-Ge with a polymer layer including Al; *5* — irradiated n-Ge with a polymer layer including Fe.

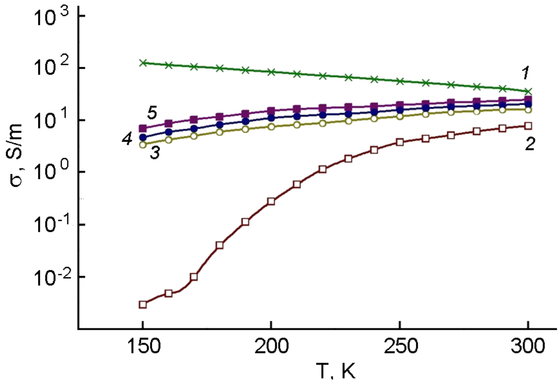

Fig. 2. Temperature dependences of specific conductivity for n-Ge single crystals, coated with a layer of epoxy composite: *1* — unirradiated n-Ge; *2* — irradiated n-Ge; *3* — irradiated n-Ge with a polymer layer; *4* — irradiated n-Ge with a polymer layer including Al; *5* — irradiated n-Ge with a polymer layer including Fe.

nitude of the field was determined by the current value through the electromagnet (current of 1 A corresponded to magnetic field of 0.2 T). Stabilized DC was supplied to contacts 1 and 2. To measure the temperature dependences of the electrical conductivity and the steady Hall effect, the sample was blown with nitrogen vapor. The temperature control of the sample was carried out using a copper-constantan differential thermocouple. During measurements, one of the ends was lowered into a Dewar vessel with a mixture of water and ice ($T = 273$ K), and the second one was fixed directly near the sample under study. The measurements of the EMF of the thermocouple and the voltage drop across the sample contacts were carried out using a digital voltmeter V7-21A.

3. Results and discussion

In [8], Hall effect measurements were performed for the n-Ge single crystals, which were irradiated by different electron fluxes with energy of 10 MeV. On the basis of the obtained temperature dependences of the stable Hall effect and the solutions of the systems of electroneutral equations, it was shown that the generated radiation defects activate two deep energy levels $E_c - 0.27$ eV and $E_c + 0.27$ eV. The filling of these acceptor levels by electrons leads to the growth of a steady Hall effect. Concentration of generated radiation defects for the electron radiation with flux $\Omega = 5{\cdot}10^{15}$ el/cm^2 proved equal to $2.8{\cdot}10^{14}$ cm^{-3}. In order to research the screening ability of a dianic resin coating with and without fillers of aluminum or iron powders under high-energy electron irradiation, the measurements of temperature dependences of electrical conductivity and Hall constant for electrons with energies of 10 MeV and flux $\Omega = 5{\cdot}10^{15}$ el/cm^2 were carried out for n-Ge single crystals coated with a layer of dianic resin. The obtained dependences are presented in Fig. 1 and Fig. 2. As follows from Figs. 1, 2, the presence of the coating of dianic resin increases the radiation stability of germanium single crystals. The samples of germanium coated with a layer of an epoxy composite with iron powder have the greatest radiation stability. According to the results of theoretical calculations [9], the average electron flux in a polymer composite is inversely proportional to the values of $B = \sum_{i=1}^{n} \rho_i \frac{Z_i}{A_i}$, and $C = \sum_{i=1}^{n} \rho_i \frac{Z_i^2}{A_i}$. Here, ρ_i are the densities of the i-th chemical element included in the macromolecule of the polymer composite, or filler; Z_i and A_i are their charge and mass numbers, respectively. The quantities $B = \rho_i \frac{Z_i}{A_i}$ and $C = \rho_i \frac{Z_i^2}{A_i}$ for the iron powder filler are larger than for the aluminum powder filler. Therefore, the transmittance of the electron beam through the epoxy composite layer with the iron powder filler is less than for the epoxy coating layer with the aluminum powder filler. This explains the greater radiation resistance of germanium samples coated with a layer of epoxy resin with the filler of iron powder in comparison to the samples of germanium with a protective layer of epoxy resin with the aluminum powder filler. A significant increase in the content of the metal filler in the epoxy polymer will lead to a decrease in the density of the composite, and consequently, to a decrease in the screening ability of the epoxy coating layer. Therefore, in our studies, the chosen content of metal powder fillers does not exceed 30 wt. parts. Calculations of the concentration of generated radiation defects were carried out for the samples studied. For this purpose, as shown in [10, 11], a system of electroneutrality equations was solved. The results of the calculations are presented in Table 1. As follows from Table 1, the presence of a protective layer with an epoxy composite without and with fillers of metal powders results in a decrease in the concentration of radiation defects formed in germanium single crystals under electron irradiation. This explains the increase in the concentration of electrons and the specific conductivity of n-Ge single crystals coated with a layer of the epoxy composite (Fig. 1 and 2, curves *3* and *4*). Also, the calculations show that the formation of radiation defects in germanium single crystals coated with a layer of the epoxy composite creates deep energy levels, E_c – 0.27 eV, belonging to the A-centers in the forbidden zone of germanium [12]. For irradiated n-Ge single crystals coated with a layer of the epoxy composite with iron powder filler, the concentration of conduction electrons and specific conductivity at room temperature do not differ much from non-irradiated specimens (see Fig. 1 and 2, curves *1* and *2*). Therefore, such a layer of the epoxy composite on germanium single crystals can serve as a protective coating against aggressive effects under irradiation with electrons up to 10 MeV.

3. Conclusions

Based on the experimental results and theoretical calculations, it has been established that the use of a protective layer of epoxy composition significantly increases the radiation resistance of germanium, especially at low temperatures. A-centers are the main radiation defects which determine the electrical properties of irradiated n-Ge single crystals, in the absence and in the presence of a protective coating layer. It is shown that the protective coating of the epoxy composite with filler of iron powder at mass fraction of 30 % and thickness of 5 mm, allows us to almost completely exclude the influence of electrons' irradiation on the electrical parameters of the investigated germanium single crystals. Thus, the obtained composites of ED-20 epoxy-dianic resin with PEPA hardener (12 parts by weight) (without fillers) and with iron and aluminum powder fillers (30 parts by weight) can be a promising material for creating low-cost protective coatings for n-Ge based semiconductor electronics elements for screening against the aggressive effects of high-energy electron radiation.

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Table. Concentrations of radiation defects in irradiated specimens of germanium, coated with a layer of epoxy composite

Sample type	Irradiated n-Ge single crystal without epoxy composite coating	Irradiated n-Ge single crystal coated with a layer of epoxy composite with PEPA hardener (12 parts by weight)	Irradiated n-Ge single crystal coated with a layer of epoxy composite with PEPA (12 parts by weight) and aluminum powder (30 parts by weight)	Irradiated n-Ge single crystal coated with a layer of epoxy composite with PEPA (12 parts by weight) and iron powder (30 parts by weight)
Concentration of radiation defects N, cm^{-3}	$2.8\cdot10^{14}$	$2.3\cdot10^{14}$	$1.9\cdot10^{14}$	$1.6\cdot10^{14}$

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