



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol.13, Issue, 12(A), pp. 2465-2469, November, 2022

**International Journal of
Recent Scientific
Research**

DOI: 10.24327/IJRSR

Research Article

NANOCOMPOSITES AND SEMICONDUCTOR DEVICES BASED ON RECYCLED RADIOACTIVE WASTE

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DOI: <http://dx.doi.org/10.24327/ijrsr.2021.1312.0504>

ARTICLE INFO

Article History:

Received 9th October, 2022

Received in revised form 21st October, 2022

Accepted 18th November, 2022

Published online 28th November, 2022

Keywords:

Recycling, Radioactive waste, Radioactive nanopowders, Radioactive nanocomposites, Radioactive semiconductor devices, Radioactive space microelectronics, Space industry.

ABSTRACT

The article provides an overview of nanocomposites and microelectronic elements used in space electronics and radiation control systems of nuclear reactors. Only those nanocomposites and microelectronic elements are taken into account that improve their characteristics in radiation fields or remain indifferent when exposed to ionizing radiation. Considering the chemical composition of the materials of these nanocomposites and microelectronic elements, it is analyzed from which radioactive materials (RM) obtained by recycling radioactive waste (RW) such composites and microelectronic parts can be made. Thus, an alternative way of radioactive waste disposal is proposed, when these wastes are used in the form of microelectronic elements designed to operate under conditions of cosmic radiation.

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INTRODUCTION

When designing devices and microelectronic circuits for space probes and planetary rovers, materials that are not sensitive to ionizing radiation are used. Or the change in the properties of materials used for space under the influence of radiation is of such a nature that these changes do not adversely affect the operation of devices and circuits. To study the radiation properties of materials, radiation sources are used in the form of radioisotope sources or particle accelerators. These sources are often difficult to access or they are expensive. The use of radioactive materials (RM) and the study of their influence on the properties of a nanocomposites or substances in which they are included, and on the quality of operation of microelectronic elements, initially completely or partially made of RM, have never been considered.

The amount of radioactive waste is constantly growing, radioactive waste storage facilities require protection and constant environmental monitoring, radioactive waste is stored for a long time (some storages are designed for millennia) (Bobrakov *et al.*, 2012). Some developed industrial countries prohibit the storage of radioactive waste on their territory at the legislative level, look for other countries, often underdeveloped ones, and build cheaper storage facilities in them, not caring about the environmental situation in these countries. Another problem that arises during the storage of RW is the risk of RW falling into the hands of terrorist organizations. Currently, there

is a strengthening in terrorist organizations both due to their coming to power in individual countries (Afghanistan), and due to association with organized criminal groups, in particular, with the drug business, which significantly increases the financing of terrorist structures, allowing them to acquire not only modern weapons (Osheev, 2018), but also, in the future, gain access to nuclear technology and radioactive waste.

The colonization of the planets of the solar system requires an increase in the number of automatic probes and planetary rovers. The equipment and structural elements of these installations operate in conditions of high cosmic radiation, so the materials from which they are made must remain with the same technical characteristics that ensure the operation of the equipment. The manufacture of equipment for space probes and planetary rovers from RM will not disrupt their functioning. The presence of already existing RW storages and the constant production of new RW can provide space agencies with RM for the production of structural materials and electronics for automatic space stations and planetary rovers. The radioactivity of RM can be comparable to or even larger the intensity of cosmic radiation. Thus, the problem of radioactive waste disposal will be solved without ecological harm to the environment and terrorist threats.

The article deals with nanocomposites with various kinds of fillers and semiconductor devices used in space technology and control electronics of nuclear reactors. The radioactive waste

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from which these nanocomposites and semiconductors can be made is considered.

Polymer nanocomposites exposed to ionizing radiation

Polymer nanocomposites with fillers from metals and their compounds - metal-polymer nanocomposites, are used in the radio-electronics and aerospace industries (Abdullah Al Naim *et al.*, 2017), (Kurbanova *et al.*, 2014), (Ismayilova *et al.*, 2017). The widespread use of polymer nanocomposites is due to the fact that the introduction of small amounts of nanomaterials into a polymer can significantly improve its physicochemical and mechanical properties.

Linear amorphous polymers of powdered polyvinyl chloride (PVC), sheet polymethyl methacrylate (PMMA) and granular polystyrene (PS) are used as electrical insulating and protective coatings, elements of electronic equipment, and various sensors for monitoring the operation of radiological systems of nuclear reactors (Gud' *et al.*, 2012). Irradiation of samples of these polymers (in the form of films 90–130 μm thick, 25 mm in diameter) at $T = 25^\circ\text{C}$ for 45 days with alpha particles with an energy of 4.777 MeV and gamma rays with an energy of 0.188 MeV from a ^{226}Ra radiation source leads to a noticeable change in the value the real part of the complex permittivity and conductivity of PS and PMMA, an increase in the electrical conductivity of PVC.

In electronics and dosimetry, high-pressure polyethylene (HPPE) films are used, which have electret properties - the ability to maintain a polarized state for a long time after removing the external influence that led to polarization (Guzhova and Galikhanov, 2017). Gamma irradiation worsens the electret properties of HPPE with a thickness of 40 to 130 μm and a size of 70×70 mm, regardless of the dose - doses from 72 kGy to 144 kGy, with a power of 1.5 kGy/h from a ^{60}Co source were used.

As can be seen from the above examples, the properties of the polymer have been changing in one direction or another depending on the irradiation dose and polymer composition. To fix the properties of polymers during their irradiation or to enhance the change in properties in the desired direction, polymer modification is used by introducing nanofillers into it. For example, the mechanical and physical properties of PVC can be improved by introducing zinc oxide ZnO nanoparticles with a diameter of less than 100 nm into the polymer matrix in an amount of 2.5 to 10% by weight, what is explained by the strong interaction of nanoparticles with the polymer (Abdullah Al Naim *et al.*, 2017). At high doses of gamma irradiation up to 40 kGy with a power of 0.34 Gy/s from a ^{137}Cs source, the PVC/ZnO (10 wt %) nanocomposite 0.12 mm thick shows an improvement in mechanical properties by almost 100% (Abdullah Al Naim *et al.*, 2017). This brings to idea the creation of initially radioactive ZnO nanoparticles from radioactive waste and embedding them into a polymer. It is known that in order to reduce the amount of metallic RW during PWR operation, the coolant of the 1st circuit is dosed with natural zinc at a concentration of 5–15 $\mu\text{g}/\text{dm}^3$ in order to minimize the radiation fields from the equipment (Maltseva *et al.*, 2017). Zinc atoms are introduced into the oxide film on the surfaces of the primary circuit equipment, forming a stable zinc spinel, which prevents the incorporation of radioactive cobalt into oxide films. When the reactor is decommissioned or the primary circuit equipment is replaced, metal RW is reprocessed, and modern methods make it possible to

completely deactivate the metal, only the radioactive slag from metal remelting is sent for disposal (Bychkov *et al.*, 2021), (Knyazev, 2021). Methods for the industrial extraction of non-ferrous metals, including zinc, from slags of the metallurgical remelting of different metals are well developed and make it possible to isolate zinc almost completely (Yunisova *et al.*, 2019), which can be used to obtain nanopowders ZnO (Zang, 2014). Since radioactive slags have not been recycled to date for the purpose of isolating the necessary compounds or elements, it is difficult to say what content of radionuclides will be in the zinc obtained in this way.

To improve the physical properties (strength and heat resistance) of HPPE, nanoparticles of metal oxides - copper and iron - are added to it (Kurbanova *et al.*, 2014). The content of metal oxides in HPPE varies from 1 - 3% wt. Irradiation of composites HPPE/(oxides of Cu or Fe) has not yet been carried out, but it is planned to be used as a heat-resistant and durable material in rocket science. Accordingly, it is expedient to create radioactive nanopowders of copper and iron oxides from metallic radioactive waste. In construction dumps contaminated with radioactive emissions from nuclear accidents or during the decommissioning of nuclear facilities, copper RW is usually represented by electrical wires. The technique for obtaining nanopowders of copper oxide has been worked out (Buyantuev *et al.*, 2010), (Zelenov *et al.*, 2020). Steel structures and equipment radioactively contaminated at nuclear facilities make it possible to obtain iron for the following production of radioactive nanopowders of iron oxide (Gervald *et al.*, 2010).

UHMWPE/SiO₂ composites (matrix of Ultra-High Molecular Weight Poly Ethylene, filler - amorphous silica nanoparticles) are used in the nuclear and electrical industries, etc. (Ismayilova *et al.*, 2017). Samples of the composite UHMWPE /SiO₂ (3-5% wt.) with a diameter of 20 mm, a thickness of 80-100 μm with spherical SiO₂ nanoparticles 20 nm in size were irradiated with γ -quanta from several ^{60}Co sources with a dose of 200 kGy, dose rate - 3.3 kGy/h. The value of the specific electrical conductivity of the nanocomposite samples increases by 5 orders of magnitude with an increase in the irradiation dose. A pure UHMWPE matrix without filler exhibits no electrical properties (dielectric).

The idea arises of obtaining silica nanoparticles from radioactive waste in order to use them as fillers for polyethylene matrices. Concrete from radioactive building dumps of structures of nuclear facilities being decommissioned, nuclear test sites, nuclear technogenic disasters can be used to produce silicon and its dioxide, because concrete contains silicon up to 30%, bound oxygen up to 50% (Pidwirny, 2006). RW stored in vitrified or cemented form in containers also contain a high percentage of silica - up to 25% in Portland cement (Gafarova and Kulagina, 2016), up to 20% in borosilicate glass (Skvortsov *et al.*, 2017). Radioactive concrete, cemented and vitrified radioactive waste can be considered as an artificial rock. To date, space agencies have worked out and are improving methods for extracting oxygen, metal and metalloids from lunar and Martian rocks (simulators of lunar and Martian regolith), for the purpose of using oxygen for breathing by personnel of alien bases, as well as a component of rocket fuel, and metals and metalloids for production needs of space colonies (Samuel *et al.*, 2015), (Bethany *et al.*, 2020), (David *et al.*, 2022). The same methods can be applied to the recycling of radioactive concrete, vitrified

and cemented radioactive waste. A brief overview of the possibility of recycling radioactive concrete and metal for the purpose of obtaining materials for space details and electronics is given in (Kizka, 2022). Silica nanoparticles can be obtained from radioactive oxygen and silicon obtained from radioactive waste recycling, by the same methods as for the production of non-radioactive silica nanoparticles (Bardakhanov *et al.*, 2008).

Semiconductor devices under ionizing radiation

Modern semiconductor elements for microelectronics are made on the basis of germanium, silicon and its dioxide. Those elements that are used in space electronics are designed taking into account their work in conditions of high radiation. It is clear that their manufacture from radioactive materials should not impair the functionality of the electronic elements. Consider some of these semiconductor elements.

The properties of germanium nanocrystals NC-Ge (photoluminescence at room temperature, long-term retention of the injected charge) make it a promising material for a new generation of nanoscale electronics that can operate under extreme conditions. These nanocrystals have been investigated for their ability to withstand nuclear particle irradiation (Issai *et al.*, 2012). NC-Ge is introduced by ion implantation into an amorphous silicon dioxide film 500-640 nm thick on the surface of a p-type silicon crystal. Irradiation of samples with high doses of fast reactor neutrons (energy up to 10 MeV) with an integral dose up to $D = 10^{20} \text{ cm}^{-2}$ led to the destruction of the crystal structure and amorphization of some of the nanocrystals, but a significant number of nanocrystals are remained. At this integral dose, devices based on bulk semiconductors are completely destroyed.

In space electronics and electronic systems of nuclear reactors, high-voltage Schottky diodes based on silicon carbide are used (Kozlovsky *et al.*, 2020). The diodes were irradiated at a high temperature up to 400°C (“hot irradiation”) with 15 MeV protons from a cyclotron. Irradiation over the entire studied temperature range had a very weak effect on the characteristics of the diodes at a dose $D = 4 \cdot 10^{13} \text{ cm}^{-2}$. Silicon carbide is obtained from silicon dioxide by, for example, heating an organic material in excess of carbon (Vlasov *et al.*, 1991) or in graphite (Yang *et al.*, 2010).

Irradiation MOS transistors based on silicon (channel) and SiO₂ (oxide between the gate and channel) with γ -quanta from ¹³⁷Cs with doses from 10 Gy to 10⁶ Gy, with a power of 0.625 Gy/s, does not affect the operation and characteristics of MOS transistors - threshold voltage, steepness of drain-gate characteristics, mobility of carriers in the channel (Aleksandrov *et al.*, 2022). The SiO₂ dielectric 0.12 μm thick for such transistors is obtained by thermal oxidation of silicon at 1000°C in dry oxygen (Aleksandrov *et al.*, 2022).

Calculation of the amount of radioactive filler

Let us assume that to manufacture a device for microelectronics, it is necessary to add a radioactive nanofiller to a polymer matrix or a radioactive semiconductor to a common semiconductor (for example, to a silicon melt from which a single crystal will be grown), respectively. Let the mass of the initial non-radioactive material (polymer matrix or silicon melt) be m_0 . Let the specific activity of the radioactive material be A_{RW} . The background activity of the non-radioactive material will be neglected. Let a radioactive material of mass m_{RW} be added to the original non-radioactive component. Then

the specific activity A_{RM} of a nanocomposite (a mixture of polymer and nanopowder) or a semiconductor melt with added radioactive material is

$$A_{RM} = m_{RW} \cdot A_{RW} / (m_{RW} + m_0). \quad (0)$$

Let the maximum absorbed dose $D_{\text{max}} [\text{cm}^{-2}]$ be known, taken as the integral flux density of ionizing particles, which does not affect the properties of the nanocomposite or semiconductor device, or changes their properties in the right direction. Let us take into account that to determine D_{max} , a sample whose thickness is on the order of microns is irradiated. This thickness is much less than the path length of ionizing particles with energies of several MeV (Gott, 1978). Both in the manufacture of a nanocomposite and the addition of radioactive material to a semiconductor, it is necessary to mix the two components, which means that it can be assumed that the radionuclides are distributed evenly over the volume of the nanocomposite or semiconductor. Then the maximum surface activity $A_{S\text{max}}$ of the resulting nanocomposite or semiconductor should be numerically equal to the maximum dose D_{max} divided by the expected operating time t_{exp} of the manufactured device under radiation conditions:

$$A_{S\text{max}} [\text{Bk/cm}^2] = D_{\text{max}} [\text{cm}^{-2}] / t_{\text{exp}} [\text{sec}]. \quad (1)$$

The empirical relationship between $A_{S\text{max}}$ and A_{RM} is taken from (Ennan *et al.*, 2011) for the case of a dispersed material:

$$A_{RM} [\text{Bk/mg}] = 0.2 \cdot (A_{S\text{max}} [\text{Bk/cm}^2])^{0.59}. \quad (2)$$

Let us substitute (0) and (1) in (2), after elementary transformations we will receive:

$$m_{RW} = \frac{0.2 \cdot m_0}{A_{RW} [\text{Bk / mg}] \cdot \left(\frac{t_{\text{exp}} [\text{sec}]}{D_{\text{max}} [\text{cm}^{-2}]} \right)^{0.59} - 0.2}. \quad (3)$$

Formula (3) makes it possible to approximately estimate the maximal amount of radioactive material m_{RW} with a given specific activity A_{RW} , which must be added to a polymer matrix or to a non-radioactive material of a given amount m_0 , so that the resulting device made from this material can withstand the radiation dose D_{max} . The maximum integral dose D_{max} should be understood now as the dose from radiation exposure due to external and internal sources of radiation.

Formula (3) has a singularity at $A_{RW} [\text{Bk/mg}] \cdot (t_{\text{exp}} [\text{sec}] / D_{\text{max}} [\text{cm}^{-2}])^{0.59} = 0.2$. This can be understood as the equality of the dose rates or intensities of external (cosmic) and internal (caused by radionuclides) radiation fields. In this case, we can take any amount of radioactive material m_{RW} and add it to the initial non-radioactive material of mass m_0 . Or even make a device only from radioactive material of a given specific activity $A_{RW} [\text{Bk/mg}]$, so that the device operates during the expected space flight time t_{exp} and withstands the radiation dose D_{max} .

If $A_{RW} [\text{Bk/mg}] \cdot (t_{\text{exp}} [\text{sec}] / D_{\text{max}} [\text{cm}^{-2}])^{0.59} < 0.2$, then this can be understood as the fact that the intensity of the external space radiation exceeds the intensity of the radiation created by the radionuclides inside the material. In this case, we take the mass modulo.

Suppose we want to make semiconductor elements for space microelectronics from silicon weighing $m_0 = 1 [\text{kg}]$. Let the time of the planned flight of an automatic space probe be $t_{\text{exp}} =$

5[years]. Let the maximum integral dose of radiation, which the microelectronic elements of the space probe must withstand, be $D_{\max} = 10^{31}[\text{cm}^{-1}]$. Let we had recycled high-level waste (cemented or vitrified RW) and extracted from it the silicon containing various radionuclides. Let the specific activity of radioactive silicon be $A_{RW} = 10^{12}[\text{Bk/kg}]$. Then, according to (3), we can add $m_{RW} = 1[\text{kg}]$ of high level radioactive silicon to the initial 1 kg of the non-radioactive silicon melt.

CONCLUSION

We considered the idea of manufacturing semiconductor devices and fillers for nanocomposites wholly or partially from recycled radioactive waste. Modern technologies in metallurgy for the processing of slags in order to extract useful elements and compounds from them, technologies developed by space agencies for the industrial processing of lunar and Martian regolith simulators, technologies for the manufacture of nanopowders and nanocomposites can be used to manufacture materials from radioactive waste for parts of micro- and radio electronics of automatic space probes and rovers. In the future, with the active colonization of the planets of the solar system, this may completely eliminate the need to store radioactive waste in terrestrial conditions. In addition, radioactive nanopowders and nanocomposites are of scientific and technical interest, since there are no works on their manufact

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