RADIATION SOLID STATE PHYSICS

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The development of the nuclear and nuclear fusion energetics, as well as of the atomic and cosmic technique, stimulated the investigation of the influence of nuclear radiation upon the solid state properties.

Related to this, in early 50-s in the USSR and abroad intensive study of the radiation defects in solids was begun. Such studies allow one to obtain an important information on the nature of the disordering structure in crystals, related to the formation of various defects and impurities, with rather sensitive and subtle quantitative technique.

Modification of properties of solids with the help of the nuclear radiation turned out to be a powerful tool for the controlled change of the solids to create materials and devices with special characteristics. In this respect the most interesting objects were semiconductors, which, among other kinds of solids, were the most sensitive to the presence of highly small amounts of defects and impurities. Various defects and impurities determine completely the electrophysical and optical properties of semiconductors, since any distortion of the periodic structure of the crystal potential, caused by the defects and impurities, leads to the appearance of the local energy levels in the forbidden band of the semiconductor and to the change of its basic properties. Wide usage of the semiconductor devices and materials in the vicinity of the nuclear power plants under the high radiation conditions required a detailed study of the nature of the radiation damage in the semiconductors and in other solid ststes.

1. Radiation defects in semiconductors

Initially it was suggested that the observed changes in the properties of semiconductors are related to the formation of almost stationary vacancies and interstitials atoms, while the irradiation process is similar to a chemical doping, when replacing atoms create a spectrum of deep levels in the forbidden band. Wide studies of the radiation defects which began in sixties, led to deep understanding of the mechanisms of the formation of simple defects, when irradiating the semiconductors by gamma quanta and by low energy electrons. It was then shown that during irradiation the elementary intinsic defects, vacancies and interstitial atoms have extremely high mobility and effectively react quasi-chemically with each other as well as with impurity atoms even at the extremely low temperatures. At the same time, from general considerations it was clear that the second stage of the defect formation (quasi-chemical reactions) should be different, when irradiating by light and heavy particles. When irradiating by gamma quanta and low energy electrons, the formation of isolated Frenkel pairs should lead to thermodynamically stable complexes of the defects with impurities. For heavy particle irradiation, when micro-regions with high density of the vacancies or the interstitial atoms are formed, the role of the quasi-chemical reactions was not clear. This was also an open question, what is common and what is different in the mechanisms of the formation of isolated defects and disordered regions, as well as how these two types of violation influence the change in the electrophysical properties of the crystal.

This made the study of the complex structure disordering, caused by the irradiation by high energy particles, in particular, by fast reactor neutrons, quite interesting. This interest was stipulated mainly by the usage of the semiconductor technique in the fluxes of fast neutrons during nuclear explosions, in the vicinity of the nuclear power stations, the reactors, and the thermonuclear devices. In this connection the "Laboratory of the non-equilibrium electronic processes in semiconductors" headed by S.M. Ryvkin was included to the Gatchina branch of the Phisical-Technical Institute, where the construction of the nuclear reactor WWR-M was began in 1956. In 1958 a special group in the Ryvkin's Laboratory was formed, which began the preparations for the studies at the reactor, at the same time studying the samples, irradiated at the atomic power plant in Obninsk, as well as at the Moscow reactors at ITEP and Kurchatov Intsitute.

The first scientific work performed at the reactor WWR-M in 1960 after achieving the 5 KW power, was our study [1] in which relative distributions of the fast neutron flux in the reactor channels were measured by semiconductor monitors.

After the WWR-M reactor achieved its nominal power the intense study of the nature of the radiation disordering in germanium and silicon, caused by reactor neutron irradiation has begun.

The main attention was paid to the study of the energy spectrum of the levels of defects, induced by fast neutrons, because just the number, the position and the character of the energy levels determine the change of all the semiconductor properties.

It was shown that at the irradiation in the reactor channels at 70° C only acceptor levels are formed in germanium and only donor ones in silicon. The absence of the donor levels in the forbidden band in germanium contradicted the data available at that time. American scientists Cleland and Crawford showed that after germanium irradiation at the reactor two donor and one acceptor levels are formed, in the duly agreement with the model considerations of James and Lark-Gorovitz about the existence of the "marginal" position of the Fermi level in the irradiated semiconductors. One could explain the contradiction by a monopolar annealing of donors, if one supposes that they can be easily annealed at 70° C. Measurements on germanium samples irradiated at the reactor at 20 C also showed the absence of radiation donors. This testified that either in our conditions monopolar donor annealing occurs much easier for some reasons than in the experiments by Cleland and Crawford, or that donors are not formed at all. In order to clarify the situation with the formation and stability of the defects, in particular, the problem of stability of the radiation donors, we have elaborated and built in 1964 a low-temperature nitrogen filled loop in a vertical channel of the WWR-M [2], which allowed us to perform irradiation at 100 K and to measure electric parameters in a wide temperature range (100-300 K), controlling the cool nitrogen supply. A portable container allowed us also to change the samples at the liquid nitrogen temperature, in order to study photoelectric, optical and recombination properties of the samples in the stationary conditions.

As a result, new data about the process of the formation and character of the radiation defects at the low-temperature irradiation at the reactor were obtained for the first time [3]. From measurements of the conductivity during the isochrone annealing in the 77 – 600 K range it was found that at the irradiation temperature of 77 K the compensation of both n- and p-types of germanium and silicon, and the Fermi level approach a middle of the forbidden band. Therefore, in the process of the low-temperature irradiation both donor and acceptor levels are embeded simultaneously. After the following heating as a result of some "ripening" maximum number of levels appears in the forbidden band. The analysis of the conductivity change and of the spectral photo-conductivity curves at each stage of the annealing allowed to determine the character of the levels found.

The analysis of the experimental data we obtained on the character of the defect formation in germanium and silicon allowed us to propose a qualitative model of the formation of the radiation defects in the irradiation by fast neutrons. According to the model, the formation of the stable defects is related to some "ripening" processes, as a result of which the energy spectrum of the levels of defects appears in the forbidden band of the crystal. The processes of "ripening" and of formation of complexes take place apparently in the all kinds of the irradiation. However, a specific feature of the neutron irradiation is that the disordered regions split mainly into the complex defects like double and triple vacancies or interstitials atoms, so the formation of the simple defect-admixture complexes (like in the irradiation by gamma quanta or by electrons) will be practically not observed.

The results of the study of the defect formation processes in germanium and silicon in the irradiation by fast neutrons were generalized in monograph [4].

2. Radiation disordering in semiconductors irradiated by high energy protons

In the middle of sixties, related to the beginning of the space studies with a piloted spacecrafts supplied with various electronic devices, the problem arose of the creation of the compact high-efficiency semiconductor devices with high radiation stability with respect to the high energy protons. The solution of the problem became possible, when powerful proton accelerators were launched at our institute (1 GeV energy) and at the Institute of High Energy Physics in Serpukhov (76 GeV energy). At that time the data on the character of the interaction of high energy protons with germanium and silicon were absent.

During 1965 – 1985 a wide cycle of studies was carried out on the character of the radiation damage in germanium and silicon, induced by protons with energies of 660 MeV, 1 GeV and 76 GeV. The results of this fundamental study were published in more than 50 papers and were generalized in monograph [5].

The analysis of the data obtained showed that, when germanium and silicon are irradiated by high energy protons, specific change of the macroscopic properties is observed, which differs from that occuring in the other kinds of irradiation. At the same time, some features of the change of macroscopic properties re semble those observed in the electron irradiation (dependence on the concentraton and on type of the initial admixture) and neutron irradiation (formation of disordered regions). Such an unusual and rather complex behaviour of semiconductor materials irradiated by high energy protons could be connected in a natural way with specific features of the elastic and inelastic interactions of high energy particles with atoms of the crystal. It was shown that the number, nature and energy spectrum of the primary and secondary particles, their space distribution, as well as the initial state of the crystal determine its final behaviour.

The results obtained allowed us to propose a classification of radiation disordering in germanium and silicon under the irradiation by high energy protons. The classification was based on the theoretical calculations of French scientists Simon and Lafond. According to the classification, three types of the disordered regions can be formed: "small" regions, like in the electron irradiation, "clusters" of defects, like those observed in the neutron irradiation, and "large spread regions", which appear in the irradiation by high energy charged particles.

The relative frequencies of the different disordering types amount to 1:10:100, so the main number of defects appearing in germanium and silicon under the high energy proton irradiation belongs to the "large spread regions", whose properties determine the basic change in the electrophysical parameters of the material in the irradiation.

At present the results of our fundamental studies of the radiation disordering in germanium and silicon irradiated by fast neutrons and high energy protons are widely used in the engineering calculations for precise controlling the properties of the semiconductors for the micro-electronics purposes, as well as to forecast and increase the stability of the semiconductor devices and microchips, working in the space or in the vicinity of the nuclear reactors.

3. Electronic properties of the disordered systems on the base of germanium compensated by the irradiation by reactor neutrons

In 70-ies a large interest in the solid state physics appeared to the disordered systems, which was caused by their wide usage in various fields of optics and radioelectronics. Together with glasses, amorphous and liquid semiconductors, to such systems belong also non-uniform crystal semiconductors, strongly doped and irradiated by high energy particles. At the beginning of our studies (1975) there existed an ample experimental material on the properties of the amorphous semiconductors and their practical employment. It was not clear, however, what kind of physical processes stipulate specific characteristics of the amorphous semiconductors related to the leap character of the conductivity, switching effects and photomemory.

It was shown in theoretic papers by Shklovsky and Efros that strongly compensated crystal semiconductors may be considered as disordered systems which can serve the simplest model of amorphous, glass and other, more complex systems.

On the basis of the wide experimental data relevant, obtained in the study of properties of germanium and silicon with radiation disordering, we showed that a new scope for the creation of the model of amorphous semiconductors arose when one used as a compensation the irradiation by high energy particles which formed the disordered regions. In this case various types of beam particles of different energies would form disordered regions of various dimensions and of various defect densities, so one can use irradiation to control spatial and energetic scale of the potential relief, as well as electronic properties of the disordered systems.

In our studies of germanium with disorderd regions, strongly compensated by fast neutron irradiation it was shown [6], that the theoretical papers by Shklovsky and Efros allow one not only to obtain the data on electronic properties and parameters of the potential relief of such disordered systems, but also new information on the parameters of the disordered regions, which was of considerable importance for the radiation solid state physics.

These studies were supported by the "Laboratory of the non-equilibrium electronic processes in semiconductors" and personally by Professor S.M. Ryvkin who helped us constantly till his departure in 1981.

4. Study of the modification of the electrophysical porperties of the HTSC-materials

A new direction in our study of the disordered systems with radiation disordering was related to the high temperature superconductors (HTSC), discovered in 1986. This was a large gift for all the physicists and we began the study of the modification of the properties of HTSC with radiation disordering in order to clarify the nature of the high temperature superconductivity. Long experience in the study of the disordered semiconductors with radiation disordering allowed us to propose a project connected with modification of properties of the HTSC materials by the irradiation by reactor neutrons.

The first measurements performed with YBaCuO-ceramics irradiated by neutrons showed high sensitivity of new superconductors to the radiation disordering and the possibility of wide modification of their properties. It was shown that the main mechanism of the radiation influence upon the structure and properties of the HTSC is the formation of the radiation defects due to the elastic scattering on nuclei.

In the oxide HTSC the main part of the defects is formed in the oxygen sub-lattice, i.e. in that part of the lattice which has the largest influence upon the superconducting properties. The estimate of the rate of the insertion of oxygen vacancies showed it to be rather large, $\approx 20\ cm^{-1}$. The study of the electrophysical properties of the HTSC materials irradiated by neutrons showed that the observed change in their properties after irradiation could not be explained unambiguously by the change of the oxygen sub-lattice due to the radiation disordering or thermal impact during irradiation (the temperature in the reactor channels is 100° C, though for some specimens it can rise to 300 − 600° C due to the gamma absorption). All this required to discern two different effects which equally change the HTSC properties during the irradiation in the reactor: thermal and radiation, the latter being connected with the formation of the disordering and structure disordering. In order to clarify the mechanism of the formation of the radiation defects one should study it at temperatures much lower than the transition temperature. For this purpose a low-temperature helium loop (LTHL) was designed and built at the WWR-M in 1991 [7]. It allowed us to measure the parameters of materials in the temperature range 20-300 K for neutron fluences up to $10^{19} cm^{-2}$. LTHL is a unique device, which has yet no analogs in Russia and in CIS. It allows one to study quasistationary disordered states and various transitional processes in solids, which occur during the irradiation in the reactor at helium temperature.

When studying the electrophysical properties of the HTSC materials (YBaCuO ceramics and films) during the low-temperature (≈ 20 K) neutron irradiation in the fluence range $\Phi = (10^{17} - 10^{18})cm^{-2}$, a "small dose effect" was found, related to the increase of the critical temperature T_c (Fig.1). A teoretical model based on the formation of two types of defects, stable and metastable ones, was proposed to explain a non-monoton temperature dependence $T_c(\Phi)$ and to obtain values of some parameters, which characterize the defects [8].

A critical current (J_c) of YBaCuO-films was studied during the neutron irradiation in the LTHL at ≈ 20 K temperature and subsequent annealing. Temperature and dose depndencies of J_c were obtained (Figs. 2 and 3).

It is shown that the radiation disordering, created by neutron irradiation, leads to the strong change in the weak intergranular linkage [9].

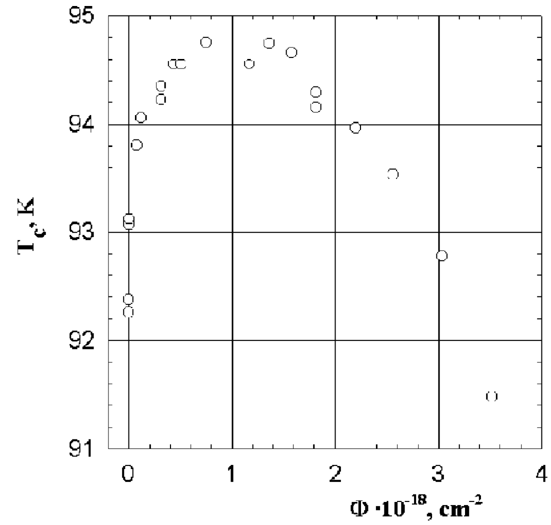

Fig. 1. Dependence of the temperature of superconducting transition (T_c) on the neutron fluence (Φ); $T \approx 20$ K

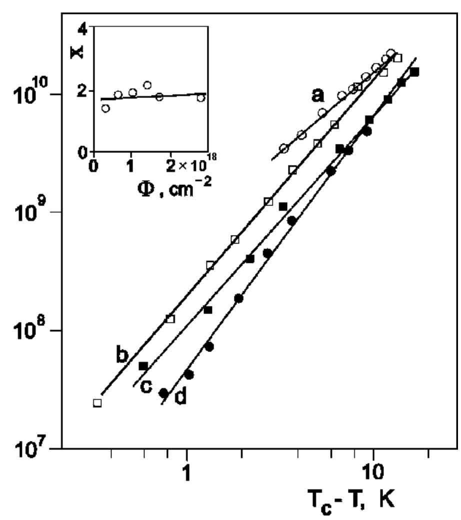

Fig. 2. Approximation of the dependences $J_c(T)=J_c^0(T_c - T)^x$ for the film YBaCuO. Shown in the insert is the exponent coefficient dependence on neutron fluences $\Phi=n_i \cdot 10^{18}$, см$^{-2}$, where $n_a= 0.3$, $n_b= 0.64$, $n_c= 1.4$, $n_d= 1.7$

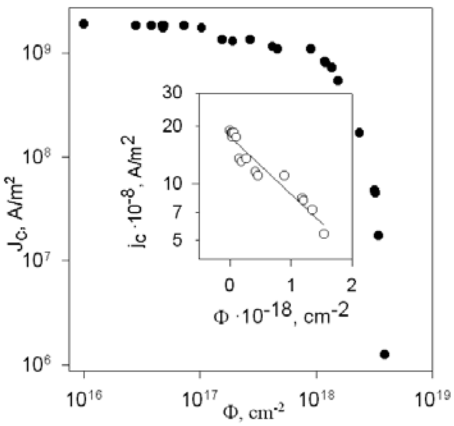

Fig. 3. Dose dependence of the critical current of the film M1. In the insert is approximation of the dose dependences by the expression Jc=Jo exp(-kΦ) , where k~1 10^{-19} cm^2

5 The study of the martencite transformations and shape memory effects in alloys during the irradiation by reactor neutrons

At present time the study is began of electrophysical and mechanical properties of the shape memory materials (TiNi, MnCu, CuAlNi) during the irradiation by reactor neutrons in the modernized LTHL at the WWR-M reactor, which allowed to measure the strain (by magnetic induced method) and conductivity of specimens under the loading in a thermocycling regime in the temperature range 150 – 450 K [10].

The alloys with martencitic phase transformations have a unique possibility of the recovery of large unelastic strain (shape memory effect) and high stress generation during the transformation. Such features make these alloys the most perspective materials to create "smart" and "intelligent" materials of the future, which combine three functions: sensor, processor and perfomer unit, lke living creatures. They are supposed to be composite materials in which one of the components is a shape memory alloy. The unusual properties of the shape memory alloys are connected with a capacity for multiple and reversible change of the crystal lattice structure under the influence of various external factors (temperature, pressure, magnetic and electric field, radiation, etc.). Our investigations showed that the materials with the shape memory (TiNi, CuAlNi) are very sensitive to the radiation. For the first time it was shown that the capacity for reversible deformation during the martencite transformation is kept up to the fluence of ≈ 10^{19} cm^{-2}. It was found that after the low-temperature neutron irradiation (15 – 450 K) the temperatures of the phase transitions are shifted to the low temperature region (Fig. 4).

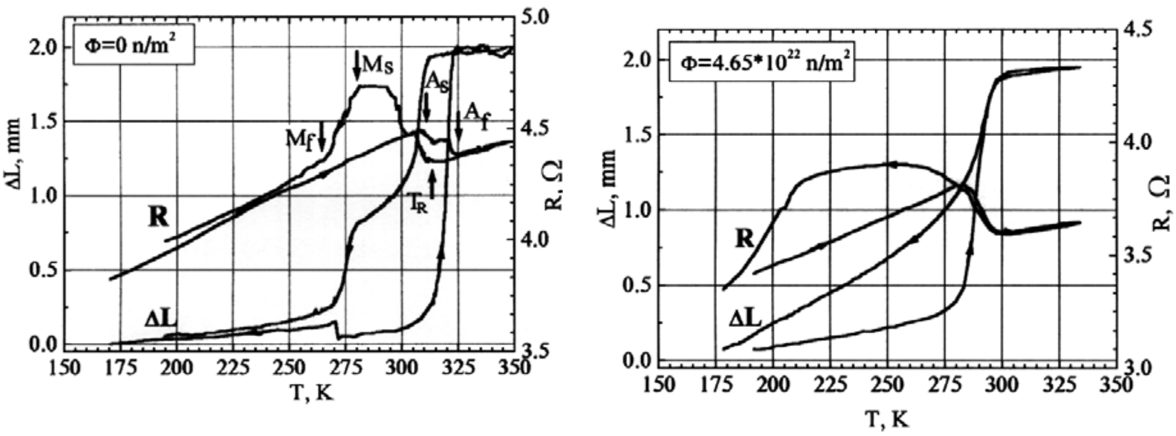

Fig. 4. Dependence of the electric resistance and deformation in the TiNi alloy on the temperature before (left) and after (right) the irradiation in the LTHL by neutrons at T=170 K. Ms, Mf are the temperatures of the beginning and the end of the conversion of austenite-martensite; As, Af are the temperatures of the beginning and the end of conversion of martensite-austenite; TR is the structural state change temperure

The regularities observed are explained by the change of the degree of long-range disorder of the crystal lattice during the neutron irradiation. These results allow one to understand the nature of physical processes which develop in shape memory alloys the during the irradiation, and could be used to create new technique for nuclear power production.

6 Low-temperature helium loop for the PIK-reactor

At present time the technical project of the low-temperature helium loop for the PIK-reactor is designed for studying the influence of the radiation upon electrophysical and mechanical properties of solids during the irradiation by reactor neutrons in a wide temperature range (20 – 1000 K).

LTHL should become a multipurpose physical setup which could provide both scientific and applied research for a wide circle of researchers from Russia and abroad. It has no analogs in the world.

Unique characteristics of the LTHL will allow one to perform a wide spectrum of both fundamental and applied research on actual problems of radiation solid state physics:

- the study of the mechanism of the impact of neutron irradiation upon macroscopic and electronic properties of semiconductors and HTSC, as well as their defect structure in the temeperature range 20 – 300 K;
- the study of the effect of the reactor radiation upon the phase transitions in solids, including the study of structure transformations in metals, segnetoelectrics, magnetic transitions in ferro- and antiferromagnetics; order-disorder transitions in alloys;
- crystallization processes in metal glass with transition temperatures in the range 200 – 1000 K;
- the study of the influence of neutron irradiation upon electrophysical properties of materials employed in atomic and thermonuclear energetics, determination of their capability and lifetime.

REFERENCES

[1] R.F. Konopleva, S.R. Novikov, Atomnaya Energia **11**, 545 (1961) in Russian.
[2] S.R. Novikov, R.F. Konopleva et al., Atomnaya Energia **20**, 245 (1966) in Russian.
[3] R.F. Konopleva et al., FTT **8**, 332 (1966) in Russian.
[4] R.F. Konopleva, V.L. Litvinov, N.A. Ukhin, *Features of an irradiation of semiconductors by high energy particles*, Atomizdat, 1971, in Russian.
[5] R.F. Konopleva, V.I. Ostroumov, *Interaction of the high energy charged particles with germanium and silicon* (Atomizdat, 1975, in Russian).
[6] R.F.Konopleva, Preprint FTI – 671, L., 1980, 26 p.
[7] A.K. Pustovoit, R.F. Konopleva et al., Preprint PNPI – 1749, L., 1991, 30 p.
[8] R.F. Konopleva et al., Superconductivity: physics, chemistry, technique **6** 568 (1993), in Russian.
[9] B.A. Borisov, Preprint PNPI – 1919, Gatchina, 1993, 28 p.
[10] S.P. Belyayev, A.E. Volkov, R.F. Konopleva, I.V. Nazarkin. A.I. Razov, V.I. Solovej, V.A. Chekanov, FTT **40**, 1705 (1998) in Rassian.