Atomic Processes in Semiconductor Crystals

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Abstract—The formation of a new field in the radiation physics of semiconductors and semiconductor technology under the general guidance and with the direct participation of the late A. V. Rzhanov is reviewed historically. This line of research gave rise to a multitude of practical applications; however, most importantly, it forced scientists to radically change the established concepts of reactions in semiconductor crystals by taking into account the mobile defect–impurity subsystem susceptible to external factors. The concepts developed form the basis for considering the processes at the atomic level, especially during the formation and modification of active clusters and nanoobjects. © 2001 MAIK “Nauka/Interperiodica”.

In this paper dedicated to the memory of Anatoliĭ Vasil’evich Rzhanov, I relate the history of the formation and development of a promising line of research, the radiation physics and technology of semiconductors; this is one of the basic research fields at the Institute of Semiconductor Physics, and is what our institute is known for and is proud of. As the leader of a large team of scientists, Rzhanov exerted a deciding effect on the problem as a whole, and also on sections of it such as the effect of accelerated particles on the surface properties of semiconductors and heterointerfaces, the doping of thin layers using ion implantation, the restoration of equilibrium in crystals by irradiation, and the formation of metastable states using pulsed treatments; for all the above subfields, Rzhanov acted as the initiator and as an active participant.

When observing radiation effects in semiconductors, researchers came across a number of unexpected, seemingly contradictory phenomena related mainly to the generation of crystal-structure defects with an accompanying modification of all the basic semiconductor characteristics, rather than to the excitation of the electron subsystem. The diversity of, and the spread in, the experimental data for various, especially multicomponent, semiconductors was so large that we would have drowned in these data had we restricted ourselves to reliable results in certain special cases. Looking back, I remember with much gratitude how Rzhanov tactfully and insistently encouraged us to change from germanium to silicon; he believed that adequate models and the basis for promising technological methods in microelectronics and nanoelectronics could be formed only when dealing with a pure and structurally perfect material.

When, in the 1950s, the problems of developing “atomic” semiconductor electric cells and doping the crystals using irradiation with particles were formulated, it seemed to many scientists that these problems could be solved easily because the foundations of solid-state physics had been well developed.

The reality was found to be much more complex and interesting; it took decades to form correct concepts of radiation-induced processes in semiconductors. Actual crystals with their nonequilibrium properties and high concentration of background impurities caused great difficulties to experimenters and necessitated the development of new experimental methods and the transition to a higher materials-science level.

The modern concepts were reached quite slowly. There are many reasons for this; however, in my opinion, the main reasons are the following.

First, it was wrongly (although, widely) accepted that elementary point defects, i.e., vacancies (the vacant crystal-lattice sites) and interstitial atoms (the atoms pushed from the sites), had low mobility.

Second, the concept of the dominant role of electronic excitations in the defect formation was automatically transferred from the physics of dielectrics to that of semiconductors.

The situation was found to be so tense and mysterious that international conferences on radiation effects in semiconductors in the 1960s–1980s were dominated by discussions of the “vacancy paradox” and “the mystery of interstitial atoms.”

The first steps were the most difficult; these were related to substantiating the hypothesis that the dominant role in the processes of the formation of active radiation-induced centers in crystals belongs to secondary reactions between the atoms forced by radiation out of the crystal-lattice sites (interstitial atoms) and vacancies and between these defects and the imperfections existing already in the crystal (impurities, dislocations, interphase boundaries, quenched-in defects, and tracks of heavy particles). The formation of complexes accounted for the appearance of many types of active radiation-induced centers with corresponding changes.
in electrical, photoelectric, optical, luminescent, and mechanical properties of crystals; however, this implied a high mobility of interstitial atoms and vacancies even at room temperature and below and, thus, contradicted the totality of traditional concepts of solid-state physics, especially the data on the thermal treatment of materials. Many scientists attributed this discrepancy to a difference between the mobility of vacancies generated by thermal treatment and by radiation. However, the standpoint according to which the vacancies are no different from each other irrespective of the method of their generation was found to be correct. However, the previous concepts of vacancy mobility were proved to be erroneous. For example, in crystals of germanium, silicon, and many other semiconductors, vacancies are found to be in a free state only during their transition from one trap (a complex) to another; the vacancy migration energy amounts to several tenths of an electronvolt and depends heavily on the vacancy charge state. It is this circumstance that led to a wrong conclusion about the low mobility of vacancies, which resulted in serious fallacies and wrong concepts.

The development of notions about the role of the second component of a Frenkel pair (the interstitial atom) was no less dramatic. The high mobility of interstitial atoms (even higher than that of vacancies), their neutrality, and the relatively low activity of interstitial-containing complexes formed the origin of a long-standing belief in (and the problem of) the “unobservability” of products of reactions involving interstitials. We had studied in detail the interaction of interstitial atoms with dislocations and interfaces and explained the effect of pushing the impurities out of lattice sites by self-interstitials; electron microscopy made it possible to observe the interstitial clusters. As a result, interstitial atoms were shown to be equal participants of the secondary radiation effects alongside vacancies; the aura of mystery around interstitials disappeared because it originated from lack of knowledge.

These were, perhaps, the most difficult and paradoxical situations and solutions to them. There were also others. It is only the discoveries of the role of energy barriers for the complex formation, the annihilation of Frenkel pairs at certain centers, and the dependence of all energy parameters and the mobility of point defects on their charge state (which, in turn, is a function of irradiation conditions and temperature) that made it possible to devise the models (at first, qualitative, and then, in certain special cases, quantitative) of radiation-induced processes.

All the aforesaid is related to structural rearrangements in crystals; these rearrangements encompass merely several atoms. Most often, the sizes of active centers generated by radiation prevent them from being directly observed. It is only the use of a combination of methods, both already known and those just developed, that made it possible to obtain the fairly comprehensive information about the properties of the primary, secondary, mobile and stable defects, and defect–impurity complexes. It is not an easy matter to list all the methods whose employment was found to be necessary to solve the problems stated above. These methods involve studies of electrical conductivity and the Hall effect; infrared spectroscopy; studies of luminescence, electron spin resonance, and photoconductivity; deep-level transient spectroscopy; studies of Rutherford backscattering and the channeling of light particles and of microhardness; electron microscopy; and so on.

At present, we have a new line of investigation that emerged at the interface between solid-state physics, the physics and chemistry of semiconductors, and atomic physics. This line, with its powerful basis of the theory of radiation-induced modifications and the methods for forming the metastable systems, gave rise to numerous practical applications. The latter include ion implantation; pulsed treatment of materials (which won the State Prize in 1988); ion-implantation synthesis; the introduction of active centers, especially, using high-temperature irradiation; the formation of disordered systems; radiation-enhanced diffusion; controlling the properties of a metal–insulator–semiconductor system; the doping of semiconductors using neutron-induced nuclear transmutations; and the enhancement of the stability of materials and devices.

Original experimental results and generalizations of them were published in several books [1–5] written by teams of authors and translated into foreign languages. The relevance of all the problems listed continues to heighten as the knowledge about actual crystals becomes more profound and as the requirements imposed on the developed devices and technologies become more stringent.

The aforementioned basic facts radically changed the established notions about reactions in crystals with the elementary structural defects involved. The modification of a defect–impurity subsystem in semiconductors became an important field of research and technological efforts.

We believe that an urgent task at present consists in extending the results of radiation physics of semiconductors to a wide field of problems in the physics of actual crystalline materials. This requires deep theoretical insight and the continuous improvement of experimental methods. Below, I dwell on two of the aforementioned problems, which have a complex history and are most general.

The first problem is related to diffusion in crystals. If experimentally observed point defects are mobile even at low temperatures, we may assume that any impurity atom at an interstice and any elementary complex of this atom with vacancies or self-interstitials (an impurity atom at the lattice site may be also considered as trapped) are relatively mobile. In this respect, diffusion is the result of repeated events of trapping and of the trapping-complexes dissociation stimulated ther-