Some physical aspects of ion implantation

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Ion implantation and related processes of deposition and sputtering.—The nonequilibrium and metastable nature of ion-implanted structures.—Amorphous solids produced by ion implantation and planar structures that include them.—Recrystallization of layers doped or (and) amortised by ion implantation.—Analysis of the composition and properties of ion-implanted planar structures.—Method of analyzing spectra of photo- and cathodoluminescence of ion-implanted layers.—Optical methods for the study of near-surface layers of ion-implanted structures.—Capacitive spectroscopy of energy levels.—Limits of applicability of ion implantation as a method of controlling properties of semiconductors and other solids.

1. INTRODUCTION

Ion implantation (II), i.e., the injection of accelerated ions into solids in order to control their properties was used at the end of 1940's by V. M. Gusev and M. I. Guseva at the Institute of Atomic Energy now bearing the name of I. V. Kurchatov in order to produce isotopic targets. R. S. Ohl[1] wrote in 1952 concerning the use of ion bombardment for improving the characteristics of point-contact germanium diodes. In the 1950's and the beginning of the 1960's M. M. Bredov, A. R. Regel', and R. F. Komarova,[2] and also V. M. Gusev, M. I. Guseva, V. V. Titov, and V. I. Kurinnyi[3,4] conducted a number of experiments in the course of which possibilities of controlling properties of semiconductors and production of p-n junctions by the II method were established. In 1954 Shockley proposed the II method as a means of controlling the properties of semiconductors and patented it in the U.S.A.[5] During the last decade this method has become widespread in microelectronics and the technology of metal-cutting instruments. In the opinion of leading specialists ion implantation and related naturally complementary methods such as depositon of thin films from a plasma and pulsed local heat treatment[1)] [6] will in the near future become basic methods in microelectronics in the production of the main types of planar devices and will lead to a radical reorganization of the electronic industry of technically developed countries.[2)]

In connection with the foregoing the question arises: what remains for physicists to do and has not the "center of gravity" of the problem moved over into the field of technology?

From the author's point of view the number of interesting directions and unsolved problems is great and is increasing rather than diminishing.

I shall attempt to draw the attention of the readers to the special features of the ion implantation process and to the physical properties of implanted solids (primarily nonmetallic ones) requiring further theoretical analysis and experimental investigation, and then in the concluding section I shall reproduce brief evaluations of the limits of applicability of the ion implantation method to nonmetallic solids.

2. IMPLANTATION OF IONS AND RELATED PROCESSES OF DEPOSITION AND SPUTTERING

Depending on the mass and energy of ions incident on a solid, in addition to ion implantation proper, i.e., the injection of ions to depths significantly in excess of interatomic distances, accompanying processes shown in the diagram of Fig. 1 will necessarily occur.[7] They can be the dominant ones under certain conditions. Figure 1 shows, purely qualitatively, the energy regions characteristic for the individual processes.

At present, as a rule, the results of ion bombardment of solids under "mixed" conditions, i.e., with exception of the case when the range of ions is very great and the sputtering of the target from the surface is insignificnt, can be interpreted only qualitatively. The process of sputtering of surfaces of solids which is being studied in detail in the USSR and in other countries has been successfully used in practice for a long time. Very recently interest has again arisen in "special cases": sputtering under the action of photons in the x-ray region and under the action of electrons of not very high energies (tens-hundreds of keV). The reason is the close relation of these processes to the processes of formation of radiation defects in the bulk of solids leading to a change in their energy spectrum and other properties, and in practice to the "degradation" of semiconductor and other solid state devices.[8]

The process of "ion deposition" is inverse to sputtering. It has been repeatedly observed and studied experimentally; interesting qualitative models exist which allow to a certain degree to interpret physical processes of the growth of metastable structures (films) from a beam of ions of not very great (10–1000 eV) energies on different kinds of substrates.

[1)]Very frequently the term "laser annealing" is used; cf., further in section 5.

[2)]The book by Ryssel and Ruge "Ion Implantation" [31] recently published in Russian translation contains a detailed description of the technology being used and of the methods for analyzing implanted structures based on silicon.

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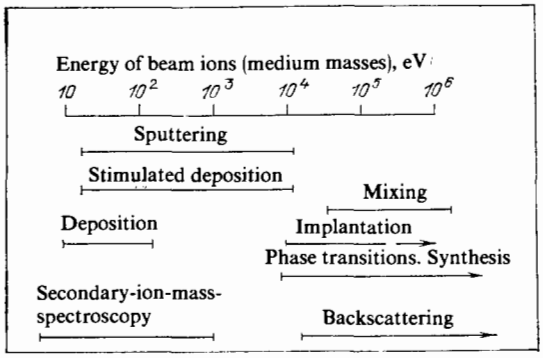

FIG. 1. Ranges of energies of ions of medium masses within which occur ion implanation, sputtering of the target and ion deposition, often accompanied by stimulated synthesis of a new phase. Also are shown energy ranges within which it is convenient to use the method of secondary-ion emission (SIMS) and of Rutherford Backscattering (RBS). In the latter case the light ions H^+ or He^+ are used. For additional information refer to Refs. 4, 6, 13, 28.

One of the interesting examples are the "diamond-like" carbon films which have lately been studied intensively in the USSR and in other countries.[9]

3. NONEQUILIBRIUM AND METASTABLE NATURE OF ION-IMPLANTED STRUCTURES

The most important feature of solids subjected to ion implantation is no doubt their nonequilibrium (metastable) condition. This circumstance has become evident already at the beginning of the 1960's. Indeed, during the very short period of time from the moment of penetration of an accelerated ion into a solid until its complete slowing down (stopping), prior to which the ion captures electrons and moves further, undergoing elastic interaction with the atoms of the target, the whole kinetic energy of the ion passes into the energy of excitation of the electronic "subsystem," the energy of thermal vibrations, and in the case of phase transitions—into the energy required for their realization. As can be seen even from, the very briefest enumeration of the possible processes, difficult and complex work is needed to describe the available experimental data and to an even greater extent to predict the probable results of future investigations.

However, the expected results, it seems to me, justify the difficulties which have to be overcome along the path of solving the *new problem* of producing stable under ordinary "working conditions" (for example, 200–700 K) solid state structures for microelectronics and optoelectronics which cannot be produced using traditional methods, for example thermal diffusion of doping impurities from the surface into the bulk of the solid. An instructive example consists of the fact that almost all the metallic alloys utilized at present are nonequilibrium ones (heat-treated or, using an older term, hardened) metals which, if they were not heat-treated, could not fulfil their functions. It should be expected that within the next few decades solid state electronics in its development will frequently be based on possibilities which significantly exceed those which could be depended upon quite recently, on the basis of those properties of solids (in the first instance semiconductors) which have been investigated in their equilibrium condition.

4. AMORPHOUS SOLIDS, PRODUCED BY ION IMPLANTATION, AND PLANAR STRUCTURES WHICH INCLUDE THEM

Starting with the work of Parsons in England and of Pavlov and his co-workers in the USSR[10,11] it was shown that ion implantation is the cleanest method of causing the phase transition of a crystal into an amorphous state. At the present time there exists a large number of experimental papers in which it is shown that ion implantation of the "like" kind (for example, Si^+ into Si) and of foreign ions under certain condtions, first of all in the case of a sufficiently high dose (integral flux), leads to the destruction of long-range order, i.e., of translational symmetry, and to the transition of a crystal into an amorphous state.

Amorphous and glass-like semiconductors, and in recent years also amorphous metals, have become the object of serious fundamental investigations and practical application.[12] Ion implantation cannot be numbered among the "cheapest," i.e. the most economically advantageous methods for producing amorphous substances. However as a result of the purity of ion beams, easily achieved by methods of mass separation, of the possibility of controlling the dose (integral flux) and of the depth of penetration of the ions which cause the crystal to go over into the amorphous state, and also of the ideal reproducibility of experimental conditions at the stages of development of amorphous solids in which the greatest clarity of understanding of the processes taking place is required, ion implantation as a method remains unsurpassed. It is important to note that a quantitative theory of making solid crystalline bodies amorphous as a result of ion implantation has not yet been constructed, and numerous experimental data are being interpreted with the aid of only partially substantiated working hypotheses. The methods of discovering implanted layers in the amorphous phase based on an analysis of diffraction pictures or on the data from the analysis of optical reflection spectra are not at all simple and require serious expenditures of effort and time.

5. RECRYSTALLIZATION OF LAYERS, DOPED OR (AND) MADE AMORPHOUS BY ION IMPLANTATION

As has been indicated above, generally speaking, all solids with implanted ions are thermodynamically nonequilibrium systems, where, as is always the case as a result of irradiation, potential energy is stored which can go over into the energy of thermal vibrations as the system goes over into a new state closer to equilibrium.

At the first stage of development of investigations and applications of ion implantation when it was established that the number of atoms displaced from their sites usually exceeds by factors of hundreds over the number of implanted atoms of an impurity in an ionic state, as a rule prolonged annealing was carried out in a furnace at a temperature which corresponds to the breaking up of complexes and intensive migration of point defects (for silicon—not lower

than 600° C). This was done in an attempt to eliminate radiation damage and to achieve maximum electrical efficiency of the implanted impurities.

Subsequently as a result of investigations of Soviet physicists in Kazan' and Novosibirsk[6] it was shown that a brief local application of intense light beams leads to a number of processes in the course of which a semiconductor or some other solid doped by ions can be brought not to thermal equilibrium, but to a new metastable state. It is well known to specialists that by this method, which at first was named by its originators "laser annealing," it is possible in many cases to produce in semiconductors "superdoped" regions in which the concentration of effective donors or acceptors exceeds the equilibrium value by factors of ten or more. In spite of their metastable nature the semiconductor and other structures produced by this method of pulsed action are frequently sufficiently stable in the required temperature range and should provide the basis for designing new devices. The nature of the physical processes in the pulsed local annealing of implanted systems has not been entirely elucidated and up to the present time gives rise to setting up more new investigations and to heated discussions associated with the difficulties in the theoretical interpretation. At all the latest conferences on semiconductor physics, papers on the subject under discussion have evoked undiminished interest. From the totality of present day data it follows that in a majority of reliably studied cases the processes of transition from the maximally nonequilibrium initial state to subsequent states are initiated by thermal (or quasithermal) excitation of atoms of the solid.

Excitation of the electronic subsystem of the solid which plays such an important role in the wide-band substances with predominant ionic coupling is not among the factors of first order of importance in the case of semiconductors (in the case of pulsed annealing).

However, it is specifically the electronic subsystem that, apparently, significantly affects such processes as diffusion stimulated by radiation and slow changes that so often become manifest in practice in the degradation of a semiconductor and other solid state devices.[8] The study of structural and other changes in layered systems obtained by the ion implantation method or by related methods (for example by deposition from a plasma in a glow discharge), as a result of pulsed or prolonged excitation by ionizing radiation (light, fast electrons), among them the hard radiation (gamma-rays), is very ncessary in order to determine the limits of applicability of pulsed annealing for practical purposes.

But what are the implanted semiconductor and other solid state structures? In order to answer this question, as a rule, experimental data are needed which can be obtained both by the usual methods of measurement and analysis of semiconductors, and also by methods which are yet to be developed.

6. ANALYSIS OF THE COMPOSITION AND PROPERTIES OF ION-IMPLANTED PLANAR STRUCTURES

a) Methods based on a controlled removal of thin layers from the surface

Among these methods one can pick out sputtering by beams of ions with energies in the range of several keV, and also by laser radiation which is often called "secondary-ion emission method" or SIMS. The sputtered material is removed into vacuum in a highly excited state: in the sputtered material, atoms and molecules of the substrate material are present both in an ionized and in a neutral state; it also contains atoms and ions of the bombarding material and products of chemical reactions which occur as a result of the catalytic action of the sputtered surface. A simple scheme of the processes taking place is shown in Fig. 2 where secondary-electron emission and photon emission are not shown on purpose, but which, generally speaking, can also be utilized for analytic purposes. The yield of secondary ions in the sputtering process, i.e., the ratio of the number of secondary particles to the number of bombarding particles under unusual conditions, for example in the case of normal incidence of 10 keV Ar^+ ions on silicon is close to unity. Thus, data on the profile of the distribution of impurities in Si at a depth of 1 μm with the density of Si atoms fo $5\cdot10^{22}$ cm^{-3} can be obtained from the spectra of secondary-ion emission in approximately one hour with the flux density of the ion current ≈ 100 mA·cm^{-2}. The sputtered spot on the surface being studied usually has a diameter of approximately 100 μm, and in order to calibrate the scale in the depth-time relationship the depths of the craters are measured directly. Figure 3 shows the experimentally determined profile for the distribution of implanted boron in Si. For impurities in crystalline silicon according to present-day data the lower limits of detecting practically important impurities are close to the following values: 10^{13} cm^{-3} (B); 10^{15} cm^{-3} (As, C, P); 10^{17} cm^{-3} (O, N); $5\cdot10^{17}$ cm^{-3} (H).

The principal complication with which one has to deal in using the SIMS method is due to the dependence of the relative yield of the impurity ions on the composition of the "matrix," i.e., the layer of the basic substance in which the impurity is "dissolved." The yield of ion depends strongly on the presence of uncontrolled impurities, on the composition of the layers adjoining the surface and on internal electric fields. Therefore, in contrast to the simple case shown in Fig. 3 in analyzing data referring to complicated multilayer

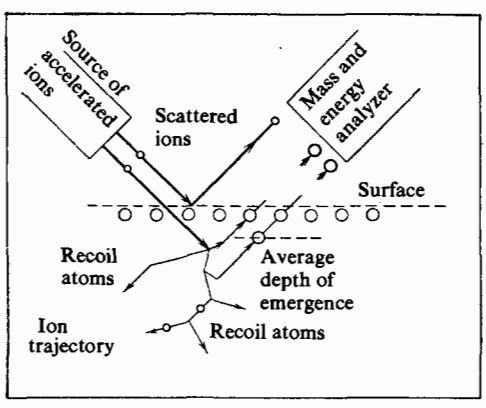

FIG. 2. Principal processes occurring upon bombardment of a solid by ions of energy of several keV.[13]

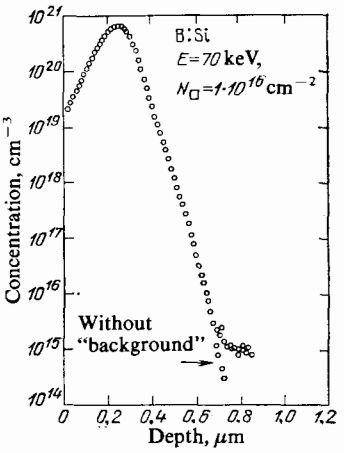

FIG. 3. Profile of the distribuiton of B atoms implanted in silicon, determined by the SIMS method.[26]

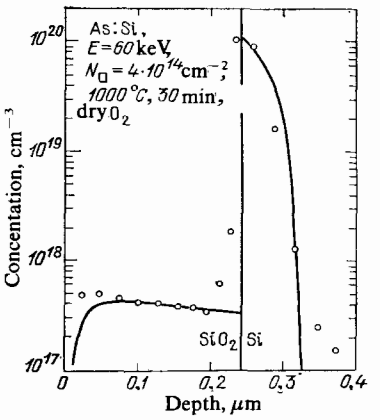

FIG. 4. Profile of the distribution of As near the separation boundary SiO_2–Si after implanting As in Si and oxidation.[29]

structures considerable errors are possible. The difficulties due to the above causes arise also in analyzing semiconductors of composition variable in depth (for example, heterojunctions in the system Ga–As–Al). In the case of very high concentrations of the impurity the yield of ions can depend on the concentration, which also must be taken into account in order to avoid error.

The composition of the neutral component of the beam of particles sputtered from the surface depends to a lesser degree on the factors mentioned above. In connection with this, recently, a technique of analysis has been developed which utilizes subsequent ionization and mass-analysis of the composition of the beam which at first was neutral.

b) Neutron activation method

This method well known to specialists and widely used in many fields is of deinite interest for specific cases when irradiation by neutrons leads to the appearance of radioactive isotopes of the implanted impurity. After irradiation from the surface of the implanted structure thin identical layers are removed step-wise with the aid of chemical etching and the presence of a radioisotope in the solution is recorded by the usual methods. As an example, Fig. 4 shows the profile of the distribution of arsenic near the separation boundary SiO_2–Si after implantation of As^+ ions in Si and oxidation under the conditions shown in the diagram. In fact this method is very close to secondary-ion spectroscopy, but can be utilized only in an appropriately equipped laboratory.

c) Analysis of a newly formed surface

After a layer of material has been removed by sputtering a new surface is opened up the properties of which can also be a source of information on the profile of the distribution of the implanted impurity. Among the various possible methods of analysis the so-called electron-spectroscopic methods deserve to be mentioned first. Emission of electrons analyzed according to energy is induced by irradiation by photons of sufficiently high energy or by excitation by an electron beam (Auger-electron spectroscopy). In addition analysis is possible with respect to the energy of the low-energy ions scattered by the surface or of the emission of photons accompanying the excitation of atoms of the surface. Except for Auger-spectroscopy the methods mentioned above so far have not been widely used. The method of Auger-spectroscopy complements the SIMS method because, particularity at a high concentration of the implanted impurity, it is practically independent of the influence of the "matrix"; however, its sensitivity is considerably lower than that of the SIMS method. Auger-spectroscopy can often be used in a vacuum installation which is basically designed for analysis using the SIMS method or in a scanning electron microscope.

The apparatus for Auger-spectroscopy consists of an electron gun for the bombardment of the sample by a sharply focused electron beam of energy of several keV, which is sufficient to remove electrons from one of the inner electron shells of the target atoms. The deep vacancy formed in this manner is filled by means of the transition of an electrom from an outer shell. The energy released in this transition leaves in the form of an x-ray quantum (which can also be utilized for the analysis) or is transferred to another electron of another shell in a process, named after the French physicist Pierre Auger, the Auger process. This process predominates in the case of excitation of atoms of the light elements. The energy of Auger electrons, just as the energy of x-ray quanta, characterizes the element the atoms of which are subjected to excitation. The mean free path of Auger electrons usually does not exceed 1 nm, which makes the method very sensitive to the composition of the atoms at the surface, compared to the analysis of the x-ray emission when the quanta emerge from depths down to 1 μm. Measuring the dependence of the intensity of the beam of emitted Auger-electrons on their energy with the aid of an analyzer one can obtain data on the composition of the surface layer. Figure 5 shows the basic processes utilized in the analysis of surfaces by the methods of Auger-spectroscopy and photoelectron spectroscopy.

One should keep in mind in comparing the results of the analysis by the SIMS method and the Auger-spectroscopy method that in the former case the data refer to the composi-

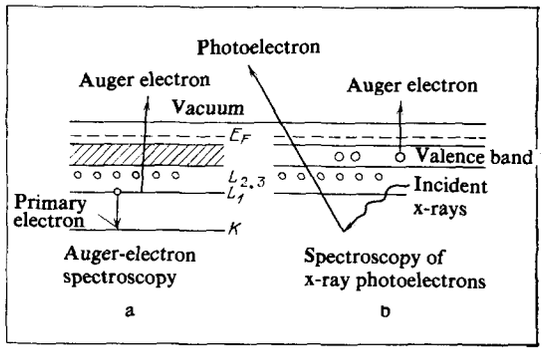

FIG. 5. Diagram of the main processes utilized for analysis of surfaces by the methods of Auger-spectroscopy and photoelectron spectroscopy.[30]

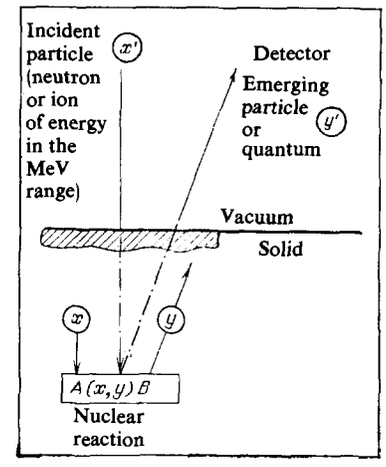

FIG. 6. Diagram of an experiment to determine the profile of the distribution of the implanted impurity by the method of nuclear reactions.[13]

tion of the ion beam sputtered by the surface and in the latter case to the composition of the surface itself. Apparently, the Aguer-spectroscoy method is more reliable to obtain quantitative data.

d) Nondestructive methods of analysis

In the majority of cases it is desirable that the changes in the properties of the sample as a result of their being measured would be minimal. Among the methods of determining the profiles of the distribution of implanted impurities usually two methods are regarded as non-destructive:

a) The sample is excited by acting upon it with deeply penetrating radiation, and the presence of an impurity is determined on the basis of the data provided by the emerging radiation (photons, particles).

b) Use is made of exciting radiation which penetrates to a quite definite depth by varying which one obtains information on the profile.

1) Homogeneous excitation

As a source of excitation neutrons or ions (H^+, D^+) of sufficiently high energy are utilized, and the distribution of the impurity is determined by the yield of the products of nuclear reactions. Nuclear interactions lead to the formation of "compound nuclei" in the decay of which gamma-quanta and particles are emitted with energies characterizing the given reaction. The energy of the reaction products usually lies in the range of millions of electron-volts.

Of particular interest are nuclear reactions accompanied by the emission of heavy products: protons or alpha-particles, in connection with the fact that they usually have sufficient energy to emerge into the vacuum, and, moreover, due to ionization losses they lose a definite fraction of the initial kinetic energy. Therefore, utilizing a spectrometric detector with good resolution one can determine the depths at which the nuclear reaction occurred. The schematic diagram of an experiment on determining the distribution profile of impurities by the method of nuclear reactions is shown in Fig. 6.

2) The method of analysis of the spectrum of backscattering of charged particles[3)]

Elastic scattering of fast charged particles by atomic nuclei is determined primarily by their electrostatic interaction (repulsion) and not by nuclear forces. The differential cross section for the former interaction is described by the well-known Rutherford formula. The principle of the method of backscattering is shown in Fig. 7.

A parallel beam of light ions of mass m and atomic number Z is incident on the surface of a solid. The energy of the ions is E_0. The energy distribution of particles that have undergone scattering at large angles is determined with the aid of a semiconductor spectrometric detector.

Elastic collisions with heavier nuclei of the material of the target M are accompanied by transfer of energy, i.e., the reflected primary particles have a lower energy $k(M)E_0$, where $k(M) < 1$, than the initial energy (E_0). The greater is the difference between the masses m and M, the less is the energy being transferred, i.e., the energy losses of the scattered particle are the lower, the greater is the mass M: $k(M_2) > k(M_1)$, if $M_2 > M_1$. If we consider an example with matrix atoms M_1, uniformly doped with the heavier impurity M_2 at a depth from the surface equal to t, then the spectrum of recoil atoms will have a structure schematically shown in Fig. 7. The greatest recoil energy will be given to ions scattered by the atoms of the impurity M_2 at the surface ($E = k(M_2)E_0$). If collisions of the same type occur at the boundary between a doped and deeper undoped region, a particle of lower energy will emerge from the surface as a result of ionization losses in being slowed down corresponding to a path of $2t$ (there and back). If the impurity atoms are distributed within the layer t uniformly, then in the spectrum there will also appear a step with a flat top, but if within the limits of the layer t a different distribution profile exists, it will be reflected in the spectrum. At energies smaller than $k(M_2)E_0 - \Delta E$, within the distribu-

[3]In foreign literature the term "Rutherford Backscattering" abbreviated as RBS is used most frequently.

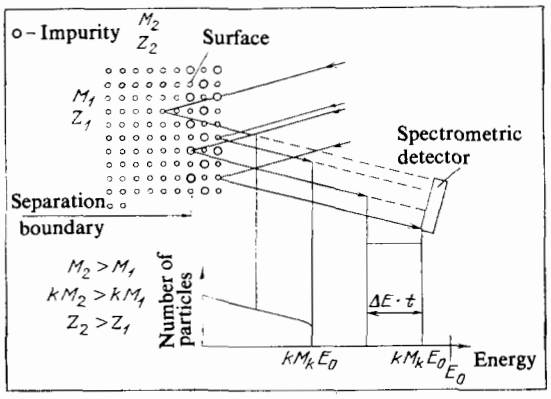

FIG. 7. The principle of the method to determine the profiles of the distribuiton of impurities on the basis of backscattering of light ions.

tion spectrum no signal from the scattered particles will be observed up to the value $k(M_1)E_0$, when signals will again appear from particles scattered by the surface of the matrix. At still lower energies a continuum will be observed from the value of the energy corresponding to $k(M_1)E_0$ down to zero energy. This region corresponds to the scattering of particles deep in the matrix down to a limiting depth from which the particles can no longer emerge.

It should be noted that within the limits of definite angles of incidence the yield of the back-scattered particles falls off sharply as a result of the channeling of the particles of the initial beam. If the incident beam is directed at a small angle to the surface then the yield of the particles scattered by the thin layer adjacent to the surface will depend sharply on how perfect is its structure (the yield is small in a perfect crystal where channeling is significant).

e) Technique of an experiment for analyzing implanted layers by the methods of backscattering, channeling and nuclear reactions[7,9,13]

The main part of the installation is an accelerator of charged particles, usually an electrostatic generator or a similar accelerator, an analyzing magnet and evacuated tubes leading into one or, more often, several target chambers, in which bombardment takes place and the scattered beam is detected. A beam of accelerated He^{++} or H^+ ions with an energy of aproximately 1 MeV and a stability of the order of ± 2 keV and a current of 10–100 nA is utilized in the majority of typical experiments.

The transverse dimensions of the beam (usually approximately 2 mm) are regulated by adjustable slits and apertures. Magnetic quadrupole lenses are used for additional focusing. The scattering chambers are provided with separate (oil-free) pumping. The sample is usually placed on a biaxial goniometer which has a stage for transverse displacements along two axes.

A spectrometric detector and a Faraday cylinder are placed within the target chamber. After amplification the pulses from the detector are analyzed by a multichannel analyzer, the signals from which are accumulated and stored in the memory of a computer. The typical time required to obtain and analyze a distribution profile is approximately 20 minutes.

7. THE METHOD OF ANALYSIS OF PHOTO- AND CATHODOLUMINESCENCE SPECTRA OF ION-IMPLANTED LAYERS

We recall briefly the features of luminescence as a research method which are significant for the study of thin ion-doped layers.

—Just as any other spectroscopic method, luminescence is "microscopic," i.e., it enables one to separate contributions from different luminescence centers (defects or impurities).

—If we are dealing with photo- and cathodoluminescence, then these methods are contact-free and (using reasonable powers of excitation) are nondestructive.

—Since the luminescence spectrum is determined by the energy structure of the centers, then in investigating it, in particular in the presence of different external effects (uniaxial compression, magnetic and electric fields), one can determine this structure and the symmetry of the center on the basis of which (utilizing data on the atomic composition, obtained, in particular, by the use of implantation) microscopic models of the centers are constructed.

—Luminescence, as a method of investigating point defects, has a high sensitivity in comparison, for example, with optical absorption and EPR. This makes it particularly attractive for the study in thin ion-implanted layers of small quantities of impurities and defects.

—Information on the microstructure of the center serves as a basis for the "luminescent spectral analysis" of solids. Following the change in concentration of known centers under different conditions of doping, irradiation and annealing, one can control the effectiveness of doping and study the processes of implantation, the mechanisms of defect formation, the interaction of defects with one another and with impurities, etc.

—The possibility of varying the thickness of the layer being investigated by changing the depth of excitation (easily attainable in the case of cathodoluminescence) is a big advantage of the luminescent method, particularly valuable in the study of thin ion-doped layers. As an example Fig. 8 shows curves of the distribution in depth of the energy losses of fast electrons (i.e., the distribution of density of produc-

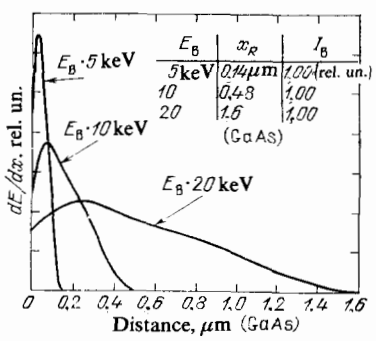

FIG. 8. Distribution of electron losses in GaAs for different electron energies E_B for the same beam current T_B. Angle of incidence 45°.[14]

tion of electron-hole pairs) in GaAs[18] with a constant electron current. It can be seen, in particular, that the use of electrons with low (≈ 1 keV) energies provides the possibility of probing a very thin layer adjacent to the surface of the crystal. Comparison of the cathodoluminescence spectra obtained with different energies of existing electrons provides information on the distribution of different luminescence centers as a function of the depth within the crystal.

Identification, i.e., the determination of the microstructure and the energy diagram of the luminescence centers is of independent scientific interest and, moreover, serves as the basis for the "luminescent spectral analysis" of solids.

The reliability of the identification of optical centers depends on the "expressiveness" of the spectrum, i.e., on the presence within it of individual features (first of all of narrow lines), which prevent it from being confused with the spectrum of another center. It is not accidental that the models of optical centers givig rise to narrow lines are the most reliable ones.

In addition to centers with deep-lying levels giving rise to wide bands of luminescence quite a number of optical centers exist with a very characteristic spectrum associated with transitions within the center and including one or several narrow lines without background and a certain structure due to the participation of phonons in optical transitions. Such spectra are usually so individual that one speaks of them as of "fingerprints" of the corresponding centers. Optical centers giving rise to narrow luminescence lines are frequently encountered in diamond,[15] silicon,[16] and according to the latest data in germanium. In III-V and II-VI semiconductor compounds the set of centers of such type is considerably more restricted and reduces practically only to impurities with unfilled inner d- and f-shells (accordingly, transition and rare earth elements) and their associations with some other impurities and defects.[17,18] Figure 9 shows spectra of Nb in GaAs,[16] and Fig. 10 shows spectra of ZnTe containing implanted ions of ytterbium at different temperatures of post-implantation annealing.[15]

Having at our disposal data on the nature of the luminescence centers it is possible to investigate the specific features of the processes of formation, interaction, and migration of point defects in ion-implanted layers. The evolution in the process of annealing of a set of defects of the lattice accompanied by a change in the state of the implanted atoms

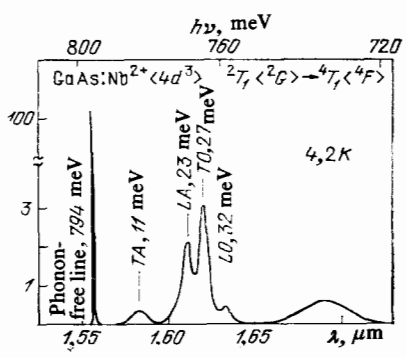

FIG. 9. The spectrum of intracenter luminescence of GaAs ion-implanted with Nb.[16]

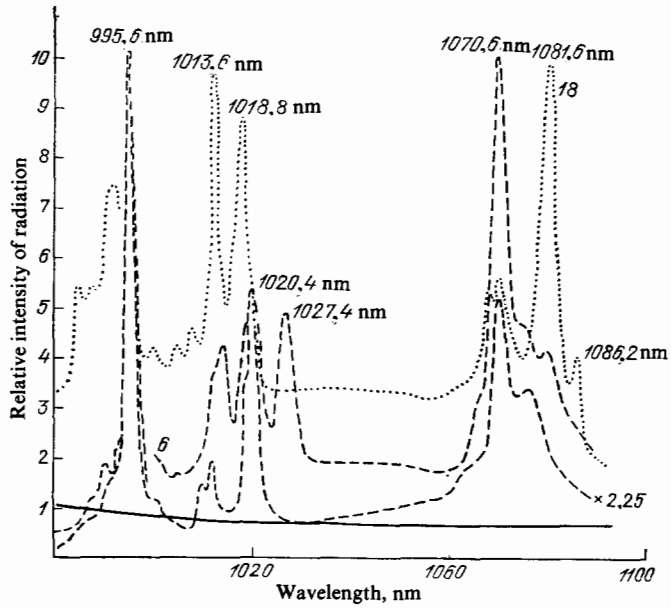

FIG. 10. The spectrum of infrared photoluminescence of ZnTe ion-doped with ytterbium ($5\cdot10^{15}$ cm^{-2}, 10 K) during annealing (solid line) and after annealing at the indicated temperatures.[19]

and the formation of complex defects including several impurity atoms and radiation defects is well illustrated by the data which refer to diamonds of type IIa (nitrogen-free) which contain implanted nitrogen atoms. In the cathodoluminescence spectra of such diamonds (Fig. 11) immediately after ion implantation (but prior to annealing) an EPR signal from single replacement nitrogen atoms is not observed. Apparently, the implanted nitrogen atoms are situated in certain internodal configurations and it is specifically with these configurations that the centers 389 and 441.5 nm are associated.

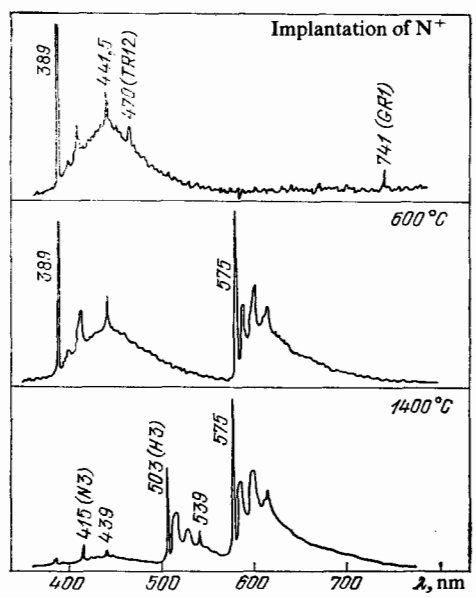

FIG. 11. The spectrum of cathodoluminescence of nitrogen-free diamond crystals after implantation with N^+ and annealing at the indicated temperatures.[20]

Thus, for ion implantation as a thermodynamically nonequilibrium method of doping, the formation of internodal, apparently, single-atomic (up to an annealing temperatures of less than 1000 °C) configurations of the introduced impurity is characteristic. Annealing at high temperatues leads to the formation of more complicated centers including two (N 2) or 3 (N 3) replacement nitrogen atoms. Ion bombardment creating a much greater concentration of defects than irradiation by electrons significantly facilitates the process of migration of impurities and defects and lowers the temperature at which formation of complexes containing nitrogen atoms begins.[19,20] For example, N_2 centers are formed in ion-doped layers already at a temperature of 1000 °C, which is less by 500° than in crystals irradiated by electrons, and less by approximately 1000° than in unirradiated crystals.

8. OPTICAL METHOD FOR STUDYING LAYERS OF ION-IMPLANTED STRUCTURES NEAR THE SURFACE

Analysis of the electrical parameters of semiconductor ion-implanted structures is associated with some difficulties. The galvanomagnetic method of investigation is often impeded by the problem of creation of ohmic contacts and the shunting effect of the substrate. In the P. N. Lebedev Physics Insitute, Academy of Science of the USSR, L. K. Vodop'yanov and S. P. Kozyrev have developed a contactless nondestructive optical method for the control of electrical and optical parameters of ion-implanted layers in semiconductors.[21] The possibilities of this method were demonstrated on a triple narrow-band compound of cadmium-mercury-tellurium (CMT).

The method is based on the mathematical treatment of experimental infrared reflection spectra taken over a wide spectral range (100–400 cm^{-1}).

The extension of classical dispersion theory to the case of a layered structure consisting of a foreign layer on an undisturbed crystalline substrate has made it possible to obtain good agreement between the calculated and measured reflection spectra. The dispersion parameters found in this manner have made it possible to determine such purely semiconductor characteristics of the implanted layer as the layer density of charge carriers, the relaxation time, and the mobility of the carriers.

Using the method that has been developed investigations have been carried out on thin layers produced near the surface in n-$Hg_{0.8}Cd_{0.2}Te$ by ion-implantation of impurities of the second (Mg, Zn, Cd) and of the third (B, Al, Ga) groups. It has been shown that directly after implantation in the dose range $3\cdot10^{12}$–$1\cdot10^{15}$ cm^{-2} the layer density of charge carriers does not depend on the type of the ion and the dose and is approximately equal to $3\cdot10^{13}$ cm^{-2}. The observed saturation effect is explained by the "fixing" of the Fermi level at the resonance level associated with the radiation effect introduced on implantation. After thermal annealing a significant difference is observed in the manifestation of impurities of the second and third groups. In the former case the electrical properties of the ion-implanted layer are determined by radiation defects, and in the latter case by the chemical nature of the implanted impurities. For the study of radiation defects arising in CMT in the range of low implantation doses an investigation was made of the dose dependence of the layer density of electrons $\Delta N_s(\Phi)$, induced by the implantation of Ar^+ ions in the layer of n-$Hg_{0.8}Cd_{0.2}Te$ adjacent to the surface. The corresponding reflection spectra are shown in Fig. 12. In the dose range of $3\cdot10^{10}$–10^{12} cm^{-2} a power-law dependence of $\Delta N_s(\Phi)$ is exhibited which reflects the fact that the radiation defect that determines the electrical properties of the implanted layer is the internodal mercury captured by intrinsic extended defects. At doses greater than 10^{12} cm^{-2}, the curve of the $\Delta N_s(\Phi)$ tends exponentially to saturation. Internodal mercury captured by thermal wedges created by radiation becomes the predominant radiation defect.

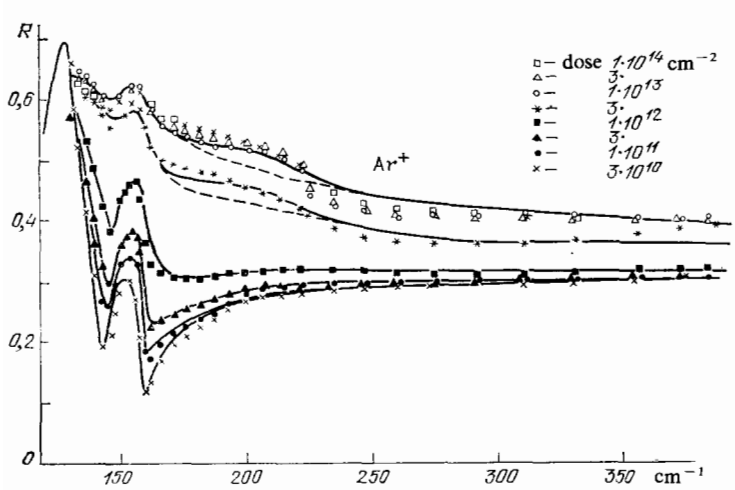

FIG. 12. Reflection spectra of n-$Hg_{0.8}Cd_{0.2}Te$ ($T = 85$ K) with implanted Ar ions at an energy of 200 keV inthe range of implantation doses $3\cdot10^{10}$–$1\cdot10^{14}$ cm^{-2}.[21]

9. CAPACITIVE SPECTROSCOPY OF ENERGY LEVELS

Thin surface layers of semiconductors subjected to ion implantation can be successfully investigated by the method of capacitive spectroscopy. G. N. Galkin and E. A. Bobrova in the Physics Institute of the Academy of Sciences of the USSR have constructed for this purpose an automated installation which enables them to carry out measurements of the volt-farad characteristics of metal-dielectric-semiconductor (MDS) structures over a wide frequency interval. Low-frequency volt-farad characteristics are recorded by using a quasistatic method.[22] This is accomplished by using a generator of a linearly variable voltage with rates from 0.5 to 0.001 v/s and deviation from linearity of $\pm 0.5\%$. The high-frequency characteristics are recorded in the frequency range of 30 kHz^{-1} MHz with the aid of a capacitance divider. The signal of the voltage across the MDS structure and the signal proportional to the capacitance of the structure are recorded with the aid of a KAMAK system into the memory of an electronic-60 computer and in order to process them in accordance with a prescribed programme they are transferred to the main frame computer GDR-11/70. The preliminary treatment of the data in the electronic-60 computer (accumulation of measurements) enables one to reduce noise significantly, which is particularly important in the case of the quasistatic method with the lowest rate of recording the characteristics. The precision of the measurement of capacity amounted to 1% for low-frequency characteristics and $\approx 0.1\%$ for the high-frequency characteristics of MDS structures with a capacitance of 300 pF. The voltage across the structure is measured with a precision of $\leqslant 1$ mV in the range $\pm$ 10 V. The programs for processing the data enable one to calculate from the volt-farad characteristics the dependence of the density of surface states at the semiconductor-dielectric boundary on the energy in the forbidden band of the semiconductor and to present this dependence in graphical form. The apparatus enables one to determine the density of surface states (DSS) in the range of 10^9–10^{12} $cm^{-2}\,eV^{-1}$. From the DSS spectra the energy position of the levels of the defects and impurities introduced by implantation is determined with an accuracy to ± 0.02 in the range ± 0.35 eV from the middle of the forbidden band of Si in the case of measurements using Si–SiO_2 structures.

This apparatus was used to make measurements on the MDS structures based on Si–SiO_2 implanted with Si, Ar^+ and other ions into the region of the Si–SiO_2 separation boundary (Figs. 13, 14, 15). As a result of investigations[23,24] of such structures energy levels have been determined for defects in Si of the *n*- and *p*- type, which do not depend on the nature of the implanted ion. The regions of temperature stability of the observed radiation defects and the dependence of their number on the radiation dose have been established, the levels of defects specific for the implanted ions have been observed, and an investigation has been made of the characteristics of the background DSS continuously distributed over the forbidden band: the amount, the law of diminuation of concentration upon annealing and the range of temperature stability.

10. THE LIMITS OF APPLICABILITY OF ION IMPLANTATION AS A METHOD OF CONTROLLING THE PROPERTIES OF SEMICONDUCTORS AND OTHER SOLIDS

a) Ranges of ions

As can be seen from the scheme in Fig. 1 theoretically there is no upper bound on energy. But in reality the implantation accelerators (in our country the term "implanters" has also already come into use) rarely permit working, particularly with heavy ions, in the energy range above 500 keV. As can be seen from the very successful approximate graph shown in Fig. 16 which was published by M. Schulz in FRG,[25] the ranges even for light ions are not very great in the absence of channeling. If a comparison is made of the numerious experimental data with the theoretical calculations,[26] it

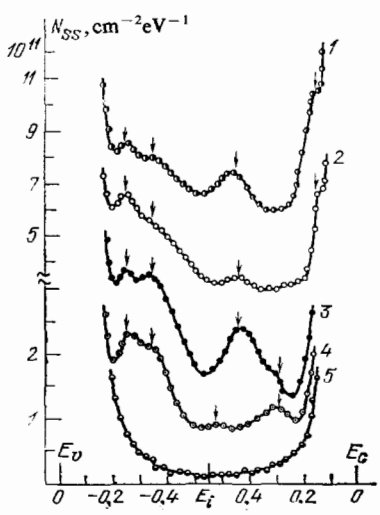

FIG. 13. Spectra of the density of surface states of structures based on n-type silicon with ion implantation with a dose of $3\cdot10^{11}$ ions/cm^2 for different temperatures of subsequent annealment.[23] 1—20 °C; 2—200 °C; 3—300 °C; 4—400 °C; 5—for a nonimplanted structure.

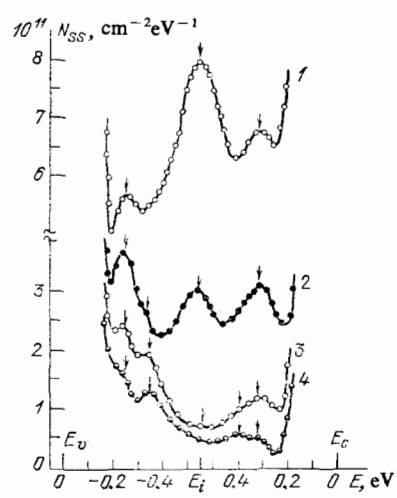

FIG. 14. Spectrum of the density of surface states of structures based on n-type silicon in the case of ion implantation after annealing at a temperature 450 °C.[24] Implantaiton doses: 1—$3\cdot10^{12}$; 2—$1\cdot10^{12}$; 3—$3\cdot10^{11}$; 4—$1\cdot10^{11}$ cm^{-2}.

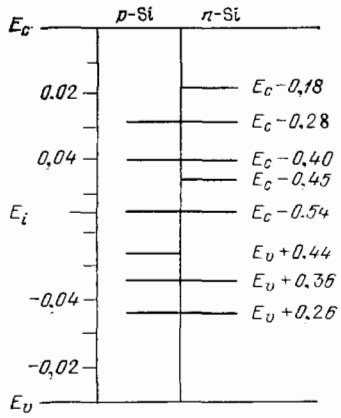

FIG. 15. Position of energy levels of states near the $Si-SiO_2$ boundary in the forbidden band of silicon arising upon implantation of Si^+ ions.[24]

can be noted that the experimental distribution profiles for the implanted atoms are always displaced into the depth of the target, although the nature of the shift is essentially different in different cases. To explain this, most frequently, use is made of concepts of "random" channeling and stimulated diffusion. First papers are beginning to appear in which after a fairly long period of skepticism with respect to the use of channeling practically interesting results are obtained.[27]

b) Limiting implantation doses of accelerated ions and realization of phase transitions

At present, particularly during the recent years, a rapid improvement of ion sources of various types has taken place. Therefore the limitation on the flux density of ions implanted in the target is determined not by the attainable current density in the beam, but by the possibilities of heat removal from the target and, particularly in the case of heavy ion and low energies, by the unavoidable sputtering of the target. It is

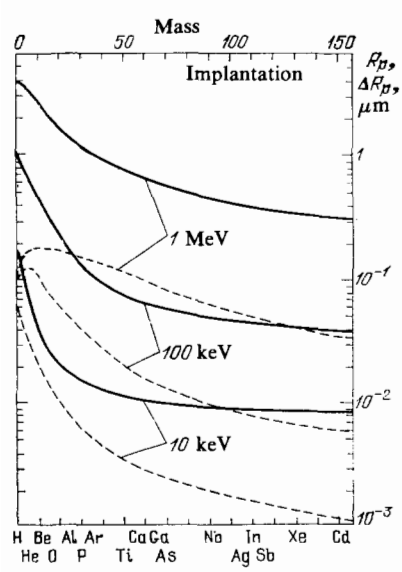

FIG. 16. Dependence of the projected range R_p (solid lines) and scatter of the ranges ΔR_p (dashed lines) in unoriented Si crystals on the mass of the implanted ions.[25]

precisely because of these circumstances that the attractive prospects of the synthesis of structures required for the investigation or for the creation of devices directly from the ion beam, circumventing the growing of crystals, cannot as yet be regarded imminent. From the specialist literature[13] and the original work, in particular, carried out in Harwell (Great Britain) it can be seen that indications of the paths towards technical improvements have been obtained which enable one to suppose that in future implantation, installations will become (in analogy to lathes and powerful x-ray tubes) "rapid-acting" and the time will come when, in any event for the solution of particular problems, the synthesis of semiconductors from pure ion beams becomes economically feasible.

c) The "purity" of the ion implantation method

In the preceding section of this review we have not considered the question of the factors which sometimes, particularly at the early stages of development of the ion implantation methods, have led to unexpected results in the analysis of the implanted layers. Under real conditions, in addition to the purity of the ion beam which can be controlled, the results can be affected by the presence of atoms of uncontrolled impurities at the surface or of atoms and molecules in the gas (vacuum) through which the beam of ions passes to the target. In order to obtain reproduceable results it is necessary to have conditions in which this phenomenon—uncontrolled implantation of atoms of foreign impurities—cannot occur. For this one requires an "oil-free" vacuum within the apparatus and a thorough cleaning of the surface prior to the beginning of implantation.

11. CONCLUSION

The aim of the present review consists of drawing attention to some of the important and far from having been solved problems in the investigations of ion-implanted systems. At present numerous groups of investigators in different countries are working in these directions. I have consciously restricted to a minimum the list of the recommended and cited literature to the most important and relatively easily available and new publications. There is a basis for hoping that both in the theoretical concepts concerning ion-implanted solids, and in the methods for investigating specific objects new paths will be found within the next few years.

The author of the review is grateful to N. G. Basov and B. M. Vul for continuous support of the investigtions of physical phenomena in ion-implanted structures within the Physics Institute of the Academy of Sciences and to his coworkers from the Sector of radiation physics of the semiconductor laboratory of the Physics Institute of the Academy of Sciences, first of all to E. A. Bobrova, L. K. Vodop'yanov, G. N. Galkin, A. A. Gippius, E. A. Konorova, V. V. Krasnopevtsev, A. V. Spitsyn, and V. A. Dravin who have provided the possibility of ultilizing in this review results published by them and who participated in the discussion of its contents.

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