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The chemistry of processes which create dielectric layers with functional group substituents on semiconductors by impurity thermo-oxidation

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ABSTRACT. Processes are examined which involve the growth of film layers with dielectric properties on the surfaces of semiconductors during thermo-oxidation in the presence of impurity compounds specially introduced into the system. It is shown in relation to the thermo-oxidation of silicon and gallium arsenide that impurities influence significantly the kinetics and mechanism of the formation of dielectric oxide layers, accelerating the process, lowering the duration of the high-temperature treatment, and altering within wide limits the composition and properties of the resulting films. The rules governing processes involving the impurity thermo-oxidation of semiconductors, determined by the class of impurity compounds introduced, were discovered. The principal criteria governing the selection of the impurities influencing specifically the oxidation process are discussed, the methods for their introduction into the system are examined, and the experimental results concerning the kinetics and mechanisms of such processes are analysed.

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I. Introduction

Thin films are used in various branches of modern technology: microelectronics, optoelectronics, laser techniques, etc. This has given rise to a new flow of information about various aspects of the creation of thin-film materials, their structure and properties, the conditions governing their preparation, and the possibility of their practical application. The development of such research has been assisted to a considerable degree by the creation of modern powerful physical instrumental methods such as electronic Auger spectroscopy (EAS), X-ray electron spectroscopy (XES) and mass spectrometric analytical methods (MSAM), including local X-ray spectroscopic micro-analysis (LXSMA), infrared spectroscopy (IRS), secondary ion mass spectrometry (SIMS), X-ray spectroscopic analysis (XSA), and other electronic-probe and optical methods. The development of studies in the field of thin films has appreciably stimulated the development of new accurate physical methods for the monitoring of the composition, structures, and properties of materials. The study of processes leading to the formation of thin films with a wide variety of properties on the surfaces of solids has greatly promoted the development of ideas about the kinetics and mechanisms of heterogeneous reactions of the solid–gas and solid–solid types.

In the investigation of the kinetics and mechanism of the formation of thin oxide films on the surfaces of solids, it was established that phenomena involving the mass transfer (diffusion and electromigration) of species through a growing film play an appreciable role in these processes. In this connection, "physical" models of the growth of films appeared, in which stress is laid on the elucidation of the nature of the diffusing species and the determination of the rate and mechanism of the mass transfer. However, the chemical aspect of the problem—the role of the chemical interaction of the components in the formation and growth of thin films—has been to some extent neglected in such research. Nevertheless, on the basis of one of the key ideas in modern chemistry, namely the dependence of the composition and properties of substances on the conditions governing their preparation and the nature of the chemical bond in them, one can solve the main problem in this science, i.e. that of the creation of new materials with specified properties.

The establishment of correlations (and ultimately of causal links) between the preparation conditions (the process conditions and process kinetics and mechanism) and the composition and properties of thin films and heterogeneous thin film structures makes it possible not only to expand the ideas concerning the chemistry of the processes but also to obtain materials with a wide range of properties. In the creation of dielectric films on the surfaces of semiconductors during their thermo-oxidation, one of the methods for the solution of this problem involves the introduction into the oxidation atmosphere or onto the surface of the support of specific specially selected impurities which, by exerting a radical influence on the kinetics and mechanism of the film growth process, can ultimately alter the composition and properties of the films in the required direction. This method can be referred to as the impurity thermo-oxidation of semiconductors. It was found that the role of the impurities introduced is unusual and that it is extremely important for it is determined not only (and not largely) by their concentration but also by their nature, i.e. one can speak of a specific effect of various impurities. This effect consists primarily in the alteration of the nature of the chemical reactions responsible for film growth, but the incorporation of impurities in the layer formed naturally influences also the kinetics of the mass transfer of the oxidant in it. Certain general rules governing the impurity thermo-oxidation processes, which were found to be universal and permitted the use of a simple approach to the creation of dielectric layers and

various semiconducting materials, were discovered and formulated in the course of the study.

Investigation of the impurity thermo-oxidation processes is based on the combination of formal kinetic studies and modern instrumental physical and physicochemical methods, which permit an unambiguous establishment of the composition of the reaction products formed, of the distribution of the components within the thickness of the layer, and of the change in the composition and structure of the layers and supports, and hence one can obtain comprehensive information about the dependence of the film composition on the formation conditions and the process kinetics and mechanisms. The application of chemical etching methods and the study of voltage–capacitance and dynamic voltage–current characteristics make it possible to establish the relation between the metal/dielectric surface structures (MDS) based on them (electrical strength, mobility of charge carriers, density of surface states, effective surface and space charges, etc.).

II. Oxidation of silicon under the influence of impurity compounds

Silicon is so far the main material in the technology of semiconductor devices and integrated circuits (IS), while SiO_2 possesses a unique combination of physicochemical and dielectric properties which gives rise to its wide scale application in microelectronics as a universal multifunctional dielectric. The formation of heterogeneous Si/SiO_2 structures can serve as a model process in the chemistry of heterogeneous reactions by virtue of the following factors:

1. The highly symmetrical structure of silicon permitting a comparatively simple modelling of the oxidation process at the atomic level.

2. The high degree of stoichiometry of SiO_2 and hence its satisfactory reproducibility with different conditions in its preparation.

3. The tendency of SiO_2 to form glasses, which rules out side effects such as the diffusion of the oxidant via intercrystallite boundaries, the segregation of impurities, etc.

4. The absence of a flux of atoms from the support to the film; as a result the oxidation proper takes place only on the moving internal interface and the silicon atoms not linked to oxygen (sometimes detected in the film).[1] This arises owing to its rapid movement and "toppling" within the support. On the other hand, when layers are deposited, the increment in thickness is ensured by the movement of exclusively the outer interface, while the support influences only the initial stages of the process (adsorption and nucleus formation). In subsequent stages, its nature does not have an effect, which permits the construction of universal models.

5. A fairly high degree of ideality of the silicon/dielectric interface and the small thickness of the transition layer. These make possible the application of the "sharp transition" model to the Si/SiO_2 heterostructure.[2]

6. The thermal silicon oxide on silicon, grown under "clean" conditions, is a kind of reference standard against which the oxide layers obtained by any other method are compared.

The thermo-oxidation of silicon itself is described by the fairly simple model of Deal and Grove[3] and also by revised models,[4–13] which yield similar kinetic equations. According to general ideas, at high temperatures film growth on a surface coated by a natural oxide ($\sim$3 nm) initially obeys a linear law where the rate-limiting stage is assumed to be the chemical reaction at the Si/SiO_2 interface. Consequently the layer of natural oxides hardly constitutes a barrier to the diffusion of oxidant species. With increase in the thickness of the natural oxide film, its barrier functions become more marked and the rates of reaction and diffusion become comparable, which corresponds to a linear-parabolic oxidation regime. Subsequently diffusion becomes the limiting factor and parabolic oxidation takes place.

However, purely mathematical difficulties, associated with the determination of the contribution of the surface reaction and diffusion to the overall process, arise even in such description. As a result of this, the effective activation energy (EAE) is assumed to be an integral characteristic of the entire process. On the other hand, the hypothesis of an abrupt change to diffusional control of the reaction is a fairly rough approximation, because under real conditions the transition from one type of control to another takes place continuously and gradually. A formal model, reflecting this gradual transition and making it possible to determine the range of temperatures and times corresponding to the change in the controlling stage and the contribution of each component within the limits of these ranges, has been proposed.[14]

Yet another problem is to incorporate as completely as possible the factors influencing the above process components. These are the nature of the diffusing species, the field and deformation stresses near the interface and in the bulk of the oxide, the generation of defects in the course of the oxidation, the influence of the degree of doping of the support, etc. Such factors have been taken into account most fully in Tiller's studies.[10–13] The establishment of the types of all the diffusing species responsible for the growth of the thickness of the layer is important.

Since fluxes of both neutral and charged oxidant species occur in the film,[8,15] it is legitimate to consider a general case—mixed diffusion and electromigration. However, such study sometimes leads to cumbersome expressions even for the oxidation of silicon itself,[16] which are relatively unsuitable for more complex processes. Despite the allowance for varying numbers of factors in different studies, the final equations describe in the general case the linear-parabolic oxidation and differ only in their coefficients.

The opposite approach proved to be extremely productive: it involves the formal kinetic description of the process on the basis of a formalised kinetic equation generalised to the maximum extent:

$$d=k^n\tau^n, \qquad (1)$$

where d is the thickness of the layer, τ the duration of its formation process, and k the integral process rate constant.

This equation does not take into account the specific mechanisms of the individual stages and characterises the process as a whole. For the oxidation of silicon itself, the exponent n varies in the range 1–0.5, reflecting the gradual transition to the diffusional control of the reaction. This relation makes it possible to describe any new layer formation processes on any supports and to carry out a comparative formal kinetic analysis.

The need to search for new dielectric layer formation processes on silicon is not at first sight dictated by practical requirements, since silicon oxide itself in general satisfies the requirements of the technology of semiconductor devices and integrated circuits. However, on passing to a flexible technology, it becomes evident that, instead of a universal multipurpose dielectric, it is in many cases useful to employ layers with properties modified for a particular purpose. The problem of reducing the duration of the

high-temperature treatment of supports and heterostructures, which makes it possible to reduce the diffusional "spreading" of the elements of the integrated circuit, remains no less timely.

The first studies on the oxidation of highly doped silicon[17,18] already demonstrated the dependence of the kinetics of the growth of films on the level of doping. Naturally, the process mechanism and hence also the properties of the films change under these conditions. Systematic study of the oxidation of diffusionally and ionically doped supports[19–29] led to the discovery of the influence of impurities in an elemental state on the kinetics and mechanism of the oxidation process and the properties and composition of the oxide layers.

Overall, the kinetic relations for the thermo-oxidation of both diffusionally and ionically doped supports are similar to the familiar relations for the weakly doped reference silicon. In all cases, the oxidation proceeds either in the linear-parabolic or the parabolic regime but its rate changes consistently: $v_{ref} < v_d < v_i$ (the subscripts ref, d, and i refer respectively to the reference process and to diffusionally and ionically doped layers of silicon). The acceleration of the process in the last two cases (by a factor of 1.5–3) promotes also the more rapid transition from the linear-parabolic to parabolic oxidation, compared with the reference standard.

The change in mechanism is manifested particularly distinctly in the oxidation in the H_2O (vapour) + O_2 mixture, where regular layers are formed in very short time intervals. Compared with ion implantation, diffusional doping does not induce appreciable disturbances in the structure of the support and one can therefore assume that the acceleration of the process is caused in this case mainly by the influence of the impurities, while in the case of ionic doping it is caused by the combined influence of the impurity and radiation defects. However, it has been established[25] that the nature of the impurity itself exerts the main influence on the rate of the process and that radiation defects are an accelerating factor only in the initial instant of the oxidation. The implantation in silicon of a chemically neutral impurity (Ar^+) hardly alters the rate of its oxidation compared with the reference standard as a consequence of the rapid annealing of the radiation defects. Furthermore, on double implantation (Ar^+ + As^+ or Ar^+ + Sb^+) the overall concentration of radiation defects is higher than in ionic doping by only one active impurity, but the rate of the process is a maximum for singly implantation.

In the cases considered, the role of the impurity reduces to the transfer of oxygen from its oxidised forms to silicon and the process is faster than the direct oxidation of the support. Interactions of the type

$$2E_xO_y + ySi = ySiO_2 + 2xE \qquad (2)$$

have been called transit interactions.[30,31] In the oxidation of doped silicon, they are most significant at low temperatures and for short process times, where the contribution of the reaction component is high and the surface concentration of the impurity is a maximum.

The similarity of the kinetics of the above processes and of the reference process is confirmed by the similarity of the exponents in the kinetic equation (1) and of the effective activation energies. There is an analogy in the process mechanisms; the increase in the complexity of the mechanism on passing from reference supports to doped and implanted supports consist only in the appearance of the parallel transit oxidation with participation of the impurity. The flux of oxidant species diffusing across the film on the inner interface (or in its vicinity) is "divided" into two: the first interacts directly with the support, whilst the second interacts via the initial oxidation of the impurity with subsequent transfer of oxygen to silicon.

The similarity of the kinetics and mechanisms of the oxidation of doped and reference supports leads to a similarity of the compositions and properties of the films obtained. They consist of virtually pure SiO_2 slightly doped by the corresponding impurity (~1–3 at.%; XSA, EAS), whose physical characteristics are also similar to those of the reference standard.

The characteristic features of the growth of films in these processes are associated with the physicochemical nature of the impurity. Thus the influence of the electron-donating and electron-accepting impurities implanted in silicon on the nature of the time variation of the process is different. Electron-donating impurities (phosphorus, arsenic, antimony) accelerate the growth of films predominantly in the initial stage, i.e. they influence mainly the reaction component. An electron-accepting impurity (boron) gives rise to a relative stability of the acceleration of the process and of the effective activation energies, which can be explained by the value of the partition coefficient of boron between silicon and SiO_2 [9] and by the possibility of not only the reaction component but also the diffusion component of the process being acted upon. This also accounts for the continuous variation of the parabolic oxidation rate constant (calculated on the basis of the model of Deal and Grove[3]) with temperature, the linear dependence of the oxidation rate on the concentration of the incorporated impurity at all stages of the process, and the difference between the kinetics of etching of the grown oxide layers compared with those for the reference standard.

The observed acceleration of the process cannot be attributed to the catalytic effect, because the latter presupposes a decrease in activation energy together with an increase in the rate. On the other hand, in the cases considered an appreciable decrease in the activation energy was not observed.

Thus the chemical effect of the impurity (the transfer of oxygen to silicon as a result of the transit interaction) plays a decisive role in the acceleration of the thermal oxidation of silicon. The impurity was introduced in the elemental form, which in fact made it possible to discover the influence of a specific element on the kinetics and mechanism of the oxidation reaction. One of the criteria governing the selection of the accelerating impurity element is the possibility of the spontaneous occurrence of the transit interaction (2), which can be assessed thermodynamically.[32] At the same time, it is necessary to take into account also the probability of other reactions competing with the transit interaction. For example, thermodynamic calculation has shown[30] that the oxides of a series of transition metals are capable of transferring oxygen to silicon. However, the metal segregated under these conditions forms silicides with the support as a result of which the reoxidation of the metal with renewal of transit is impossible. On the other hand, the introduction of the same metal directly into the support immediately leads to the formation of silicide phases. It is for this very reason that, despite the fact that the typical oxidation catalysts are in fact certain transition metals and their oxides, in the given instance it is hardly possible to identify the catalytic effect. For this reason, the results of a number of studies[33,34] in which a strong catalytic action of transition metals (Pt, Pd, etc.) was allegedly noted, are susceptible also to another interpretation: the formation of silicide phases and the breakdown of the laminarity of the flow when silicon is in close contact with the metallic needle.

The use of impurities in the form of binary compounds is more fruitful, because we then have the possibility of the action of both components of the impurity—the cation- and anion-forming agents—on the kinetics and mehanism of the process, and their effects can be not only independent but also cooperative. By selecting different classes of compounds with the same cation-forming agent (or anion-forming agent), it is possible to discover the general features characteristic of the given class as well as the characteristic features determined by each component of the impurity separately, which permits the modification of the properties of SiO_2 in several ways at once. Oxides participate in the transit interaction and when they are used as impurities it is possible to obtain a kind of reference standard for the elucidation of the role of the anion. Furthermore, the oxygen anion is one of the few species whereby the impurity can be introduced into the system in two ways: via the gas phase (unlimited source of impurity) and by deposition on the oxidisable surface of a layer whose thickness can be regulated (limited source). This is necessary to elucidate the influence of the method of introduction of the impurity into the system on the kinetics and mechanism of the growth of layers.

It has been established that, when oxides are introduced into the system, the transit interaction in a pure form determines the acceleration of the process only in those cases where the impurity oxide is indifferent with respect to the growing SiO_2 layer. Thus oxidation in the presence of Ga_2O_3 and In_2O_3 [35] is characterised by virtually the same kinetic parameters as the processes on the reference silicon or slightly doped silicon ($n = 0.5-1$, similar effective activation energies and similar acceleration of the process compared with the reference standards). The composition of the layer approaches that of SiO_2 (IRS, XSA), but the inclusion of a certain amount of gallium (indium) in the films has a positive effect on their electrophysical characteristics.[36]

If the impurity oxide is miscible and is capable of forming vitreous layers, i.e.

$$mE_xO_y + nSiO_2 = mE_xO_y \cdot nSiO_2, \quad (3)$$

then the kinetics differ sharply from those for the reference standard and for the purely transition processes. Thus, when the oxides B_2O_3, PbO, Sb_2O_3, and Bi_2O_3 are introduced into the gas phase,[37–40] the acceleration is by a factor of 50–600. As a rule, the effective activation energies are high (reaching 950 kJ mol^{-1}) and the values of n can be both smaller than 0.5 (0.3) and greater than 1 (up to 2.16). The latter is due to reactions which lead to an increase in the thickness of the layer both on the inner and outer interfaces. The layers obtained are silicate glasses of different elements (IRS, XSA, LXSMA). In the vicinity of the inner interface, impurities (B, Pb, Sb, Bi) were detected, which confirms the occurrence of the transit reaction (2).

Thus two parallel processes—transit and vitrification—contribute to the accelerated increase in the thickness of the film. Whereas in the reference oxidation or oxidation of highly doped specimens, it was possible in the first instance to identify a sequence of stages and in the second to ignore the oxidation itself, considering only the accelerating factor (diffusion of the oxidant–transit–oxidation of the impurity element–renewal of transit), in the presence of two parallel accelerating processes, each of which proceeds via a series of consecutive stages, it is necessary to introduce the concept of the determining process.[41] This is the fastest of the parallel processes which makes the greatest contribution to the increment in the thickness of the layer. The latter addition is significant, since the fastest of the parallel processes may have no bearing on the increment in the thickness and as regards kinetics it will not be determining [for example, the diffusion of the element produced by reaction (2) into the support or the film]. Since the determining process is a multistage one, it is useful to identify the rate-limiting stage in it as the slowest in this sequence.

Clearly the determining process in oxidation with participation of impurities is either the transit reaction (oxidation of highly doped silicon; after the introduction of Ga_2O_3 and In_2O_3) or vitrification (in the presence of B_2O_3, PbO, Sb_2O_3, Bi_2O_3). The transit reaction is always limited by the diffusion of the oxidant [either O_2, or H_2O (vapour), or E_xO_y] to the inner interface via a film whose properties are similar to those of SiO_2. In the determining vitrification process, the rate-limiting stage is also the mass transfer of E_xO_y. However, here this proceeds not via SiO_2 but via a silicate glass of the given element having a less ordered and looser structure, which greatly accelerates the rate of transfer. Furthermore, in the experimental temperature range certain impurity oxides (PbO, Bi_2O_3) may be in the fused state, which also facilitates the mass transfer of E_xO_y.

The method used to introduce the oxide into the system without affecting significantly the process mechanism (the number of stages, their nature, and their sequence) greatly influences the rate of increase in the thickness of the layer (and hence also the kinetic characteristics). Evidently, in the oxidation of Si/E_xO_y structures with a layer of oxide deposited on the surface both the determining process and its rate-limiting stage are the same as in the previous case. The characteristic features of the procedure are as follows: (1) the transit interaction develops already in the initial instant at a high surface concentration of the impurity at the silicon/oxide interface generated; (2) the latter factor ensures an intense transit reaction with overlap of the local superheating fields;[42] (3) the mutual diffusion of the components in the vitrification process through the dense impurity oxide layer formed beforehand is hindered compared with mass transfer through the loose silicate film of the given element formed during the introduction of the impurity through the gas phase; (4) apart from the parallel consecutive process considered, which ultimately promotes an increase in the thickness of the resulting film, it is essential to take into account the competing process involving the evaporation of the deposited impurity film and leading to a decrease in its thickness. As a consequence of these causes, exponents $n < 0.5$ as well as somewhat reduced effective activation energies are characteristic of oxidation reactions of the Si/E_xO_y heterostructures.

Thus, when the reaction leading to the mutual dissolution of the oxides (vitrification) is possible, it in fact ensures the main increment in the mass of the film and is the determining process on which depends also the composition of the resulting layers. The possibility or impossibility of the transit reaction and of vitrification are determined primarily by the nature of the cation-forming element.

The method of introduction of the impurity into the system is as a rule dictated by the type of the anion-forming impurity element. The sulphides of Group IIIA–VA elements can be usefully deposited directly on the oxidisable silicon surface, because the evaporation of these compounds at the high temperatures (and in an oxygen medium) used in the growing of the films, is impossible without decomposition and chemical reaction. In other words, it is useful to create a limited source of the impurity.

The rate of increase in the thickness of the layers in the thermo-oxidation of Si/E_xS_y is the same as for Si/E_xO_y; the exponents n are less than 0.5 (0.12–0.40) and as a rule decrease in the course of time (to 0.05); the effective activation energies are 140–540

kJ mol^{-1} depending on the nature of the cation-forming impurity element and the process stage.[36] The Si/E_xS_y heterostructures are oxidised in two or three stages. In the first stage, the deposited sulphide layer is transformed in accordance with the sulphide–sulphate–oxide sulphate–oxide scheme (IRS, XSA, LXSMA). Bearing in mind the high temperatures of the thermo-oxidation of these heterostructures, it must be emphasised that, since this stage is limited by the diffusion of oxygen through a very loose sulphate–oxide–sulphate layer, it is completed very rapidly and it is as a rule possible to record the increment in the thickness of the layer starting from the second stage. By this instant, the front of the migration of the impurity oxide (as the final sulphide oxidation product) reaches the support and ensures the transit reaction.

We may note that oxides forming part of the composition of the oxide sulphate phases are also capable of entering into similar reactions. The transit reaction is the determining process in the oxidation of the Si/E_xS_y heterostructures for which the sulphide oxidation products do not form vitreous layers with SiO_2. The growth of the film is then limited by the given stage, for example, as in the Si/In_2O_3 heterostructures with $n_{av} = 0.13$.[43] Here the rate-limiting stage is the mass transfer of the impurity oxide, bound in the film (limited impurity source) to the internal interface; in the absence of vitrification, it is hindered and the process acceleration rapidly decays with time. The resulting layer consists of the impurity oxide and the concentration of SiO_2 increases only in the vicinity of the inner interface (XSA, IRS, MSMA). Some migration of SiO_2 from the inner interface to the outer one has apparently a favourable effect on the formation of bridge bonds and the "healing" of defects. The resulting layer therefore consists of a dielectric film, although In_2S_3 is in fact a semiconductor.

If vitrification is possible, then it is added to the above sequence, i.e. it follows the transit reaction. In this instance, the above process is in fact determining and leads to the formation of the silicate layer of the given element (IRS, XSA, MSMA, LXSMA). It is limited by the mass transfer of the impurity oxide, forming part of the composition of the deposited film, to the inner interface, which is faster than the analogous process in the absence of vitrification. This stage is in fact the first of those recorded (after the rapid oxidation of the deposited sulphide layer) for the Si/GeS_2, Si/PbS, Si/Sb_2S_3, and Si/Bi_2S_3 heterostructures.[44–47] Here the values of n are 0.22–0.40 and the effective activation energies are 180–240 kJ mol^{-1}.

The process does not terminate in the formation of a silicate framework of the given element because the impurity oxide incorporated in it is capable of mass transfer (rate-limiting stage) and a further transit reaction (determining process), which ultimately leads to the formation of a silicon oxide framework (IRS, XSA). The transfer of the impurity component, bound up in the network of the silicate glass of the given element, is more strongly inhibited than in the previous stage, although most of it is present in the form of the oxide. The formation of the silicate framework of the element is therefore rapid and that of the silicon oxide framework is much lower. Very low values of n (0.18–0.05) correspond to this stage and the effective activation energies are 240–540 kJ mol^{-1}.

The characteristic features of the processes considered depend also on the type of the cation-forming element. If the vitrification is limited, then the mass transfer of the impurity is strongly inhibited and the transition from the silicate framework of the element to the silicon oxide framework is difficult, so that the latter can hardly ever be detected in a pure form in the temperature and time range investigated. This is the situation in the oxidation of the Si/GeS_2 heterostructure, where the solubility is limited in the $SiO_2–GeO_2$ system.[44] On the other hand, antimony forms the most thermally unstable sulphide in the series considered and hence in the oxidation of the Si/Sb_2S_3 heterostructures the competing process involving the evaporation of the deposited sulphide is most marked, appreciably reducing the thickness of the deposited impurity layer in the initial instant of the oxidation.[46]

The stability of bismuth oxide sulphates gives rise to a definite arrest in the process in the sulphide layer oxidation stage.[47] On the other hand, the fastest conversion of the sulphide into the oxide takes place in the case of lead. This factor, together with the vigorous occurrence of reactions (2) and (3) as well as the facilitated mass transfer of the impurity oxide in the loose network of the lead silicate glass lead to the virtually instantaneous formation of the lead silicate framework and to the rapid replacement in the latter of the lead oxide component by the silicon oxide component.[45]

Thus the thermo-oxidation of the Si/E_xS_y structures makes it possible to obtain dielectric layers with a high rate of growth (acceleration by a factor from 5 to 60). The anion-forming agent (sulphur) ensures the gradual development of the process and the formation of the resulting layers under milder conditions than those established in the oxidation of Si/E_xS_y structures and also in the presence of oxides in the gas phase. On the other hand, sulphur is absent from the final product, evaporating predominantly in the form of SO_2 during the conversion of the sulphate into the oxide. On vitrification in the system, the oxide is fully consumed in the transit reaction; part of the impurity element produced in reaction (2) diffuses to the support, while another part diffuses into the film and then evaporates. In the impurity process considered, one can therefore obtain relatively pure silicon oxide layers with a satisfactory quality[36] and over a short period.

The idea of introducing anions into the film, where they are retained and ensure a change in its properties in the required direction, is undoubtedly fruitful. Here preference should be given to chlorine. A number of studies have been published[48–52] in which the influence of chlorine on the properties of silicon/oxide layers and heterostructures was demonstrated. It involves a decrease in the instability of the MOS† structures [metal oxide structures?], an increase in the lifetime of the minority carriers in the silicon support and in the electrical strength of the films, a decrease in the density of surface states at the Si/SiO_2 interface, and the suppression of the generation of packing defects and their "healing".

Taking into account the foregoing factors, it is useful to introduce chlorine together with the cation, i.e. to employ oxidation with participation of impurity chlorides. Here too the type of the anion-forming element determines the method used to introduce the impurity into the system—evaporation from the gas phase. The chlorides of the Group IIIA–VA elements employed are comparatively volatile and can be readily introduced into the gas phase, while it is almost impossible to use the method involving their deposition on a support because of their high chemical reactivity and tendency to hydrolyse.

Despite the fact that at high temperatures the impurity chlorides employed undergo pyrolysis and pyrohydrolysis to different extents in an oxidising medium (which contains in addition an undetermined amount of water vapour), the difference between the kinetics of the oxidation reactions of silicon on evaporation from the gas phase

† MOP in Russian (Ed. of Translation).

[sic!] [into the gas phase?] of impurities with the same cation-forming agent (oxides and chlorides) makes it possible to regard the involvement of the latter in "chloride" transit

$$2ECl_x + O_2 + Si = SiO_2 + 2E + xCl_2, \quad (4)$$

$$(4/x)ECl_x + 2H_2O + Si = SiO_2 + (4/x)E + 4HCl. \quad (5)$$

The thermodynamic feasibility of these reactions is one of the criteria governing the choice of the impurity chlorides and at the same time the choice of the oxidising medium. Thus reaction (4) is thermodynamically impossible for $GaCl_3$ and $InCl_3$ and the oxidation of silicon in the presence of these oxides therefore takes place in a H_2O (vapour) + O_2 mixture. On the other hand, if both reactions are impossible, then the chloride can be used in the form of an impurity merely for the introduction into the gas phase of a volatile compound of the given impurity (provided that the vapour pressure, for example, of the chloride, is much higher than that of the corresponding oxide), subject to the condition that the pyrolysis and pyrohydrolysis of the chloride take place preferentially in the system, while the oxide transit reaction (2) is thermodynamically feasible.

The thermo-oxidation of silicon in the presence of chlorides ($GaCl_3$, $InCl_3$, $SbCl_3$, $BiCl_3$, $PbCl_2$, $GeCl_4$, and PCl_3) [53-59] takes place in a linear-parabolic regime. For $GaCl_3$, $InCl_3$, $SbCl_3$, and $BiCl_3$, the determining process is reaction (4) or (5) whose rates are limited by the mass transfer of the chloride fragment across the growing layer. Under these conditions, there are countercurrents of chlorine or hydrogen chloride formed at the inner interface in the course of these reactions and responsible for the breaks observed in the growing films.[36] The latter facilitate to a certain extent the transfer of the impurity to the reaction surface. The grown films consist mainly of SiO_2 slightly doped with chlorine and (to different extents) with the impurity cation-forming agent (IRS, XSA, XES, EAS, LXSMA). The presence of chlorine in the vicinity of the inner interface (XES, SIMS, LXSMA) demonstrates the occurrence of the chloride transit reactions (4) and (5). If reaction (2) plays a decisive role in the growth of the films, then the film will probably have been partly etched by chlorine and hydrogen chloride—the reaction products derived from the chlorides—in the vicinity of the outer interface.

The degree of doping of the films by the cation-forming agent and the acceleration of their growth compared with the reference standard (process characteristics) are determined in this instance also by the nature of the cation-forming element. The acceleration is ~1.5 for $GaCl_3$ and $InCl_3$ and ~2 for $SbCl_3$ and $BiCl_3$. This is caused by the possibility of reaction (3) for $SbCl_3$ and $BiCl_3$. The tendency towards vitrification is most marked for bismuth and the level of doping of the films with bismuth is highest (XSA, LXSMA). However, the concentration in the given processes of impurity oxides as secondary oxidation products of the elements produced by reactions (4) and (5) is low. Thus the physicochemical characteristics of the cation-forming elements (Ga, In, Sb, Bi) are responsible for the nature of the determining process and hence of its controlling stage.

In the range of comparatively low oxidation temperature (750–950 °C), the principal accelerating agent in the growing of films in the presence of lead chloride[57] is the impurity introduced initially. It has been established that at these temperatures most of the $PbCl_2$ passes to the specimen being oxidised in a chemically unaltered state. For the given process, it is possible to identify the following sequence: (1) mass transfer of the impurity chloride to the inner interface; (2) transit interaction of type (4) with participation of $PbCl_2$; (3) oxidation of the lead generated in the transit reaction; (4) type (3) vitrification. Since the resulting film consists of a lead silicate glass (IRS, LXSMA), the determining process in this stage is the mutual dissolution of the oxides [reaction (3)], which, however, is limited by the mediating effect of the mass transfer of $PbCl_2$ from the outer to the inner interface. In the loose film of the lead silicate glass, this process is not greatly hindered, as is indicated by the value of the exponent n close to unity (n_{as} = 0.84).

The oxide forms of lead, which are the products of the interaction of $PbCl_2$ in the gas phase, exert the main influence on the kinetics and mechanism of the oxidation reaction in the range of high temperatures (1100–1200 °C). The nature of the determining process (vitrification) is retained in this stage and the rate-limiting stage is the mass transfer of PbO to the inner interface. At moderate temperatures (1000 and 1050 °C), the reactive reactants are simultaneously lead chloride and lead oxide.[57] $PbCl_2$ creates the most favourable conditions in the given process for the rapid formation of films. The acceleration of film growth is a maximum (by a factor of 22) in the range 750–950 °C and a minimum (by a factor of 3–5) in the range 1100–1200 °C, whilst in the range 1000–1050 °C the acceleration has intermediate values (by a factor of 6–12). Chlorine has been detected (LXSMA) in the films corresponding to the low-temperature stage, which, together with presence of lead in the support (XSA, LXSMA), constitutes proof of the occurrence of the chloride transit reaction (4).

The nature of the cation-forming elements determines the relative stabilities of the chlorides over the entire experimental temperature range ($GaCl_3$, $InCl_3$, $SbCl_3$, $BiCl_3$) or in a particular portion of it ($PbCl_2$) and hence are responsible for the definite influence of the impurity introduced initially on the characteristics of the growth of films and their properties.

On the other hand, $GeCl_4$ and PCl_3 [55,56,58] undergo virtually complete pyrohydrolysis already in the gas phase and are converted into the corresponding oxides. The latter give rise to a flux of the impurity in the film, the mass transfer of the $Ge(P)_xO_y$ fragments limiting its growth as a whole. At advanced stages of the process, vitrification is the determining reaction (IRS, XSA); on the other hand, at the beginning there is a possibility of an "induction" period where the film growth (process with $GeCl_4$) is determined by the finite rates of pyrohydrolysis of the chloride and of the deposition of the corresponding oxide on the support and also by the limited miscibility in the E_xO_y–SiO_2 system. These features of the processes arise from the properties of the cation-forming impurity elements, which exhibit the most marked non-metallic properties in the series of chlorides considered and hence form unstable chlorides.

The change in the mechanism of the thermo-oxidation of silicon after the introduction of impurity chlorides into the gas phase compared with the reference oxidation[3,18,36] and thermo-oxidation in the presence of the halogens and hydrogen halides,[48] on the one hand, and the growing of films in the presence of oxides, on the other, leads to an appreciable difference between the properties of the films. Thus, in the "chlorine" and "hydrogen chloride" oxidation, chlorine is known to be concentrated in the vicinity of the inner interface,[60] while in the cases examined above films comparatively uniformly doped with impurity cation and chlorine were obtained (XES). Under these conditions, there is a change in the kinetics of the etching. For example, the magnitude of the mobile charge changes by an order of magnitude (for $SbCl_3$ and $BiCl_3$; there is no charge on $GeCl_4$, $PbCl_2$, and PCl_3) and there is

also some decrease in the surface charge and in the density of the surface states. However, the last two characteristics are poorer for the chloride processes examined than for the "chlorine" and "hydrogen halide" processes, because the inner interfaces are disturbed and there is an increase in the degree of defectiveness of the films caused by the reactions (4) and (5), the evolution of gaseous products, and breaks in the direction of the outer interface.

III. Impurity thermo-oxidation of gallium arsenide

The foregoing ideas concerning the involvement of impurities in the formation of oxide layers on silicon can be largely extended to other semiconducting materials, in particular, to compounds of the type $A^{III}B^{V}$. The main principle of the selection of the impurity from the standpoint of its ability or the ability of its derivatives to participate in the transit transfer of oxygen is applicable also in this instance. On the other hand, determining processes of the second type (vitrification) do not play a significant role here, because such a process is retarded at the low oxidation temperatures characteristic of the compounds $A^{III}B^{V}$. Nevertheless, the mutual dissolution in the oxide systems $A^{III}_2O_3-B^{V}_mO_n$, $A^{III}_2O_3-E_xO_y$, and $B^{V}_mO_n-E_xO_y$, which is appreciable in many instances, can promote the improvement of the properties of dielectric layers, diminishing their defectiveness.

Compared with silicon, the oxidation of gallium arsenide, the most important of the compounds of the type $A^{III}B^{V}$, has a number of characteristic features which hinder the formation of high quality dielectric layers. Firstly, it is impossible to identify the sequence of processes, because the diffusion of oxygen to the support is always accompanied by the diffusion of gallium and arsenic into the film. Thus, there are always countercurrents of the components in the film. Under these conditions, the reactions ensuring the increment in the mass of the layer are possible not only on the inner interface but also on the outer one, as well as in the bulk of the film. Secondly, the evaporation of the volatile component of the support (arsenic) is responsible both for the imperfection of the semiconductor/dielectric interface and for the increased defectiveness of the growing film. The degradation of the support necessitates in its turn the application of comparatively low temperatures in the oxidation of GaAs at which the transport processes investigated are greatly retarded. Thirdly, thermodynamic calculation has shown,[64] that the thermo-oxidation of GaAs proper is itself a transit process because, on being oxidised, arsenic subsequently transfers oxygen to gallium:

$$As_2O_3+2GaAs=Ga_2O_3+4As, \quad (6)$$

$$3As_xO_y+2yGa=yGa_2O_3+3xAs. \quad (7)$$

Hence the thermodynamically stable pairs are Ga_2O_3-GaAs and Ga_2O_3-As.[62] The arsenic reduced in the course of the transit reactions (6) and (7) proper is concentrated on the inner interface and exerts a negative influence on the properties of the metal/dielectric surface structures (MDS structures) obtained subsequently.[63] The above features are responsible for the complexity of the composition of the layers obtained and also for its marked dependence on the process parameters. In the general case, the film grown on GaAs during its thermo-oxidation consists of Ga_2O_3, As, As_2O_3, and $GaAsO_4$,[62,64,65] the first of the above components predominating in layers obtained under not unduly severe conditions.

Thus impurity transit is essential for the acceleration of the oxidation of both the gallium and arsenic components of the support in order to increase the rate of formation of the layer consisting predominantly of Ga_2O_3 and to increase the efficiency of the oxidation of arsenic, promoting thereby its segregation in the film in an oxidised and not elemental state. The latter factor ensures the "healing" of defects and the improvement of the properties of the films and the MDS structures.[66]

The postulate of the transit interaction, put forward above, involving the oxide forms of the impurity as the main factor accelerating the oxidation of the supports in which impurity ions have been implanted was confirmed also for gallium arsenide. It was established that antimony implanted in GaAs accelerates the oxidation of the latter, that boron does not increase the rate of growth of films, and that phosphorus retards it.[67] These features are correlated with the results of thermodynamic calculations for the corresponding transit processes and the available information about the physicochemical properties of impurity oxides.[68] As for silicon, it has been found that the kinetics of the thermo-oxidation reactions of gallium arsenide doped with antimony ions and of the reference process are similar. However, for the Si/SiO_2 heterostructure the partition coefficient of antimony is such that it is mainly concentrated at the inner interface, while in the corresponding gallium arsenide/oxide heterostructures antimony is segregated in the film (EAS, SIMS, MSMA), which has a favourable influence on the electrical strength of the latter. This is apparently caused by the interaction of the oxide forms of antimony with Ga_2O_3 and As_2O_3 (IRS).

The thermo-oxidation of GaAs when the gas phase contains impurity oxides (GeO_2, SnO, PbO, Sb_2O_3, Bi_2O_3, V_2O_5) capable of the transit interaction

$$(3/y)E_xO_y+2GaAs=Ga_2O_3+(3x/y)E+2As, \quad (8)$$

$$(3/y)E_xO_y+2Ga=Ga_2O_3+(3x/y)E, \quad (9)$$

also ensures the acceleration of the formation of the films.[69-71] The acceleration is by a factor of between 2 and 26 depending on the type of the cation-forming impurity element. The resulting films contain mainly Ga_2O_3 and are weakly doped with arsenic and impurity oxides (XSA, MSMA, IRS, SIMS).

The influence of the oxides GeO_2 and SnO on the kinetics of the thermo-oxidation of GaAs is similar. This is caused by the characteristic features of the evaporation of the above impurity compounds. The rate of oxidation in the linear regime is smaller for both processes compared with the parabolic regime (n = 0.28 and 0.40). According to Tananaev and Shpirt,[72] the evaporation of GeO_2 entails the formation reactions of GeO, Ge_nO_n, and Ge (the products of the disproportionation of GeO), which reduce the surface concentration of the impurity in the initial instant of the oxidation reaction. In the process with participation of SnO, the main influence is apparently exerted by the polymeric Sn_2O_2, Sn_3O_3, and Sn_4O_4 molecules, which make an appreciable contribution to the overall pressure of the impurity vapour; however, they are formed as a result of a complex series of reactions,[73] which is in fact the reason for the induction period.

The films obtained are weakly doped with the impurity component, in contrast to the layers grown in the presence of PbO, Sb_2O_3, and Bi_2O_3 (XSA, EAS, IRS). Lead, antimony, and bismuth are incorporated to the greatest extent in the growing layer, but, compared with the element silicate glasses obtained in the

corresponding processes on silicon, their concentration is low (from 1 to 6 at.%; XSA, MSMA, EAS), which confirms the retardation of the mutual dissolution of the intrinsic and impurity oxides caused by the nature of GaAs and the corresponding oxides. The appreciable accelerations obtained (by a factor of up to 26) indicate the decisive role of the transit interactions (8) and (9) in the film formation processes involving all the oxides investigated. The transit reaction can proceed preferentially at the inner (Sb_2O_3, n = 0.77) and outer interfaces and also in the bulk of the films (PbO, n = 1.4; advanced stages of the processes with GeO_2, SnO, Bi_2O_3, n = 1.10–2.17). Since the main component of the layers obtained is Ga_2O_3, the rate-limiting stage is apparently in all cases the diffusion from the support into the gallium film, such a film being essential for the formation of films both by the impurity-transit mechanism and in the course of the parallel process of the oxidation of the support itself.

The creation of a restricted source of the impurity by depositing the corresponding oxides on the oxidisable GaAs surface leads, as for silicon, to values $n < 0.5$ (for the GaAs/PbO, GaAs/Sb_2O_4, GaAs/Bi_2O_3, and GaAs/V_2O_5 heterostructures, n = 0.01 to 0.42 [74,75]),which corresponds to the interactions in the solid phase. At the inner interface, the impurity oxide transfers oxygen to the gallium of the support already in the initial instant. The impurity element produced thereby diffuses both to the support and to the film and undergoes further oxidation. There is also simultaneous diffusion of gallium into the deposited E_xO_y layer, which is responsible for the transit reaction both at the outer interface and in the bulk of the layer. The rate-limiting stage is the diffusion of gallium. The resulting layers consist mainly of the impurity oxide containing Ga_2O_3, arsenic, and its oxides (IRS, EAS, XSA).

Thus, while the determining process and the rate-limiting stage are apparently identical for the unrestricted and restricted impurity sources, there is also a fundamental difference. In the former case, gallium diffuses in a layer whose composition is similar to that of its own oxide, while in the latter it diffuses into the pure impurity oxide. The formation of Ga_2O_3 in the oxidation of the GaAs/PbO heterostructures in argon,[74] the presence of the impurity element in the support, and the steady increase in the Ga_2O_3 content on moving from the outer to the inner interface (XSA, EAS) demonstrate the occurrence of the transit interactions. Again the retardation of the transport processes and the extremely low oxidation temperatures employed preclude, as in the case of silicon, the transition from the impurity oxide layer to a weakly doped intrinsic oxide.

It is quite important that an accelerated formation of films can be achieved on gallium arsenide in the presence of transition metal oxides, in particular V_2O_5. In the oxidation of the GaAs/V_2O_5 heterostructures, not only the acceleration of the increase in the thickness of the layers (by a factor of $\sim$6) but also an appreciable decrease in the effective activation energy compared with the value for the reference process has been observed, which makes it possible to interpret the process mechanism as catalytic. In this case, the method of introduction of the impurity into the system is evidently also extremely important. Thus, when V_2O_5 is introduced into the gas phase (an unrestricted source of impurity), there is no decrease in the effective activation energy and the determining process is the transit reaction, as for other impurity oxides. Only for a restricted impurity source are there possibilities for the development of the process via a heterogeneous-catalytic mechanism (contact between two solid phases along the entire surface, creating a high concentration of surface-active centres and possibly ensuring the coverage of the local superheating fields).

A similar retarded growth of films compared with the parabolic regime (n = 0.075–0.43) has been observed also for the thermo-oxidation reactions of the gallium arsenide/sulphide heterostructures.[76–80] Here the anion-forming impurity element determines, as already mentioned, the main features of the process and the method of introduction of the impurity into the system. Because of this, a similarity is manifested between the processes considered and the oxidation of the analogous silicon structures. The intensity of the chemical interactions in the heterostructure being oxidised depends on the nature of the semiconductor matrix. Thus the main bulk of the layer grown by the thermo-oxidation of the GaAs/In_2S_3 heterostructure consists of In_2O_3.[76] Here the transit reaction is fairly feeble because of the similarity of the chemical properties of Ga_2O_3 and In_2O_3 and also because of the low process temperatures. For the same reason, the content of antimony in the films grown by the thermo-oxidation of the GaAs/In_2S_3 heterostructures (as well as heterostructures with other deposited sulphides) is higher than in the analogous layers grown on silicon (XSA, SIMS, EAS, LXSMA). The increase in the gallium content in the vicinity of the inner interface (in the oxidised form) as the process develops (XSA, EAS) reflects the increase in the contribution of the transit interaction to the overall process. It is of interest to note that, compared with the relatively pure reference oxides, these films are enriched in silicon, which indicates a higher miscibility in the As_2O_3–In_2O_3 systems compared with As_2O_3–Ga_2O_3.[68]

In the layers obtained by the oxidation of the GaAs/E_xS_y heterostructures at comparatively low temperatures, it is possible to detect simultaneously all the products of the oxidation of the sulphide (XES). Here the determining process is the transit interaction of these products (the oxide and oxide sulphate forms) with the gallium of the support, which is limited as a rule by the diffusion of this component. Thus the films grown by oxidising the GaAs/GeS_2 heterostructures[77] contain GeO_2 and $Ge(SO_4)_2$ as well as Ga and As. As the process develops near the inner face, there is a steady increase in the Ga_2O_3 content and a decrease in that of GeO_2, which demonstrates the occurrence of the transit reaction. If the decrease in the concentration of the impurity oxide component were caused by the competing evaporation process, the ratio of its concentrations in the outer and inner layers would have been the reverse of that observed.

The layers obtained by the thermo-oxidation of the GaAs/PbS heterostrucures[78] contain lead in the form of $PbSO_3$ (XES). Apparently it is in this instance a secondary product of the interaction of PbO (formed on oxidation of the sulphide) with the SO_2 evolved. The presence of PbO in the system and the occurrence of the transit reaction are indicated by the presence of elemental lead in the support (XSA). The oxidation sequence of the deposited sulphide layer is clearly manifested for the GaAs/Sb_2S_3 heterostructure.[79] Antimony oxide as well as antimony sulphite are present at the outer interface; deeper layers contain the impurity sulphate and the incompletely oxidised impurity sulphide (XES). $Bi_2(SO_4)_3$, Bi_2O_3, and gallium and arsenic oxides have been detected in films grown by the thermo-oxidation of the GaAs/Bi_2S_3 structures (IRS, XSA).[80] In all the layers obtained in the presence of the sulphides of Group IV and V elements on the surface of gallium arsenide, the concentration of gallium is higher compared with the analogous films obtained by the oxidation of GaAs/In_2S_3, which indicates a greater contribution of the transit reaction and its decisive role.

Indeed, as already emphasised, the transit reaction in the $GaAs/In_2S_3$ heterostructure is relatively ineffective and hence the increment in the thickness of the layer (n = 0.075) is correspondingly very small; for $GaAs/GeS_2$, its probability is higher and n is now 0.21. The highest values of n occur for the GaAs/PbS (0.42), $GaAs/Sb_2S_3$ (0.43), and $GaAs/Bi_2S_3$ (0.35) heterostructures, in which there are conditions for an extremely vigorous transit reaction and in addition mutual dissolution is observed (IRS) in the $Ga_2O_3-E_xO_y$ systems. Together with the presence of large impurity ions (especially of lead and bismuth) in the bulk phase, this factor facilitates the mass transfer in the film. This feature and also the vigorous transit reaction actually explain the increased content of gallium in the given layers compared with the layers grown by the oxidation of the $GaAs/In_2S_3$ heterostructures.

The formation of arsenic sulphides at the inner interface, observed in the thermo-oxidation of the GaAs/PbS and $GaAs/Sb_2S_3$ heterostructures (XES), is especially important. This suggests that not only the oxygen transit reactions examined but also direct anionic transit takes place. Such transfer of sulphur from one component to another promotes the binding of arsenic and prevents the evaporation of arsenic, the degradation of the inner interface, and the penetration of arsenic into the resulting layer in a free state. For this reason, the electrical strength of the layers increases by a factor of 5–10 compared with the reference oxide, while the density of the surface states decreases severalfold.

Thus the same main kinetic features are manifested in the oxidation of the $GaAs/E_xS_y$ heterostructures as in the processes on the corresponding silicon structures: low values of n, the gradual occurrence of the interaction of oxygen with the sulphide film, and the occurrence of a competing evaporation process from the outer interface.

A common feature of the $GaAs/E_xS_y$ oxidation processes is the decisive role of the impurity oxide transit limited by the diffusion of gallium, which is indicated by the extremely high effective activation energies for the process, close in order of magnitude to the reference values. Naturally, the composition of the resulting layers is determined in many respects by the characteristics of the semiconductor matrix, which determines the oxidation regime. In the case of gallium arsenide, the successive conversion of the deposited sulphide into the oxide with subsequent transit interaction is retarded. This makes it possible to detect in the film various sulphide reaction stages but does not enable one to achieve a transition of the sulphide film–film oxidation products type and the interaction with the intrinsic oxide phases—the intrinsic oxide weakly doped with the impurity.

The features of each process examined above are determined by the nature of the cation-forming impurity. In particular, for the $GaAs/Sb_2S_3$ heterostructures the deposited layer, transformed during the oxidation process, hinders the diffusion of gallium to the least extent and the concentration of the latter near the outer interface is highest (XSA). Since the oxidation of the sulphide begins at precisely this boundary, the concentration of the oxide forms of the impurity is a maximum in this region and best conditions are created for the transit interaction. Furthermore, the similarity of the properties of the oxide in the $As_xO_y-Sb_xO_y$ system ensures to a certain extent their miscibility, while gallium antimonates are apparently formed in the $Ga_2O_3-Sb_xO_y$ system (by analogy with arsenates). This is in fact the reason why the acceleration of the oxidation of these heterostructures is greatest (by a factor of $\sim$20).

The influence of the cation-forming impurity element is revealed most strikingly in the thermo-oxidation of gallium arsenide in the presence of chlorides, whose introduction into the gas phase is actually determined by the nature of the anion-forming element. It was already emphasised above that $PbCl_2$, $SbCl_3$, and $BiCl_3$ are stable in an oxidising medium even at the high temperatures used to grow the films on silicon.[81,82] These compounds actually ensure a flux of the impurity to the support in the oxidation of gallium arsenide when they participate and enter into the chloride transit reaction:

$$2ECl_n + 4Ga + 3O_2 = 2Ga_2O_3 + 2E + nCl_2. \quad (10)$$

As in all the previous cases, there is simultaneous oxidation proper of the support by oxygen. The chloride transit reaction is determining, because, on the one hand, the process is accelerated relative to the reference process (by a factor up to 230) and, on the other, the process kinetics differ appreciably from those of the process in the presence of the oxides of the same elements where the oxide transit reaction is determining. The determining process is in the general case limited by the diffusion of gallium atoms bound initially in the support. The process thus controls the reaction on the outer interface to an even greater extent, because of the source of the impurity is unrestricted and the mass transfer of ECl_n in the gas phase takes place at a high rate.

The characteristics of the processes depend on the nature of the cation-forming agents. Thus the oxidation in the presence of $PbCl_2$ and $BiCl_3$ proceeds in the linear regime owing to the loosening of the resulting layer and the facilitation of the mass transfer in the latter.[81,82] This fact is not only responsible for the acceleration of the diffusion of gallium and of the impurity chloride fragments but also promotes the rapid outflow of arsenic from the inner interface, which also limits the hindrance to the transfer of gallium. Antimony, on the other hand, enters the layer in such small amounts apparently owing to the rapid diffusion in the film and evaporation in the form of the oxide produced in the transit of the element from the outer interface. On the other hand, the inclusion of a certain amount of antimony in the film does not promote its loosening and does not create conditions which prevent the accumulation of arsenic at the inner interface. These factors retard the diffusion of gallium and the film grows the linear-parabolic regime.[82]

Depending on the process characteristics, the composition of the layers also varies (IRS, XSA). The films grown in the presence of $PbCl_2$ are doped with the impurity to the greatest extent; they constitute complex formations which are the products of the interaction of Ga_2O_3, PbO, and As_2O_3 and contain also oxide chloride fragments. The layers grown in a medium with $BiCl_3$ are fairly weakly doped with bismuth, but their arsenic content is increased apparently as a result of the miscibility in the $As_2O_3-Bi_2O_3$ system. Oxidation in the presence of $SbCl_3$ results in the formation of Ga_2O_3 films weakly doped with antimony and chlorine.

The characteristics of the cation-forming elements are responsible for the instability of the chlorides $GaCl_3$ and $InCl_3$. After the introduction of $GaCl_3$, n = 1.63 and the effective activation energy is only 6 kJ mol^{-1} for the oxidation process.[83] This is a virtually non-activated process and such parameters indicate the occurrence of physical adsorption.[84] Thus in the given instance the determining process is the deposition on the support of a layer of Ga_2O_3 formed during the reactions

$$ECl_3 + H_2O = EOCl + 2HCl, \quad (11)$$

$$EOCl + 2H_2O = E(OH)_3 + HCl, \quad (12)$$

$$2E(OH)_3 = E_2O_3 + 3H_2O. \quad (13)$$

In this instance the growth of the oxide film is virtually unlimited, since the mass transfer in the gas phase is rapid. Naturally the resulting layer consists of Ga_2O_3, which, however, is strongly doped with arsenic (IRS, XSA). The competing arsenic evaporation process is suppressed, because the rate of growth of the layer is so high that it inhibits kinetically the diffusion of arsenic to the outer interface and hence its evaporation in the form of oxides.

On introduction of $InCl_3$, the deposited In_2O_3 layer, formed by reactions (11)–(13), is capable of entering into a transit interaction with the gallium of the support. This process is determining,[85] since, for the high value of the exponent n at an advanced stage of the process (n = 1.57), the effective activation energy is likewise high (110 kJ mol^{-1}) and is close to the corresponding reference value. This means that the rate-limiting stage is the diffusion of gallium. Here film growth takes place on two interfaces ($n > 1$) and on the outer one the pyrohydrolysis of the chloride makes an appreciable contribution to the increment in film thickness. The resulting layer consists mainly of In_2O_3 containing chlorine and also of gallium and arsenic oxides (XSA, MSMA, SIMS). The vigorous interaction in the $In_2O_3-As_2O_3$ oxide system ensures the "healing" of the defects in the In_2O_3 semiconductor and sharply increases the electrical strength of the layers (by more than two orders of magnitude) compared with the films grown on GaAs under relatively clean conditions.

Thus, taking into account the characteristic features of the cation-forming elements under the conditions employed, the chlorides examined can be divided into two groups—stable and unstable. Within the framework of each group, the similarity of the cation-forming elements leads to the similarity in the behaviour of their chlorides in the oxidising medium. However, the fact that gallium is one of the components of the support whilst the derivatives of indium interact both with the components of the support and with their oxide forms is responsible for the difference between the mechanisms of the formation of the layers and hence of their properties.

IV. Characteristic features of the effect of impurity compounds on the thermo-oxidation of indium phosphide

The following conditions must be maintained for the formation of impurity oxide layers with a satisfactory quality on semiconductors: (1) the impurity introduced initially or its oxidation products must ensure the acceleration of the formation of layers via the transit or catalytic mechanism; (2) the mutual dissolution of the intrinsic and impurity oxides, possibly with formation of compounds (silicates, arsenates, etc.) is desirable; (3) in the presence of the quantities of the cation-forming agent listed above, the anion-forming agent should improve the properties of the layers ("healing" the defects, neutralising the charge in the film, etc.); (4) in the oxidation of semiconducting compounds with a volatile component, it is desirable to create a restricted source of impurity in the form of a deposited film; (5) the optimum chemical binding of the volatile component of the support by the anion-forming impurity element (and not the cation-forming element, since in this case the "metallic" nature of the inner interface is more marked).

These general conditions are applicable also to semiconducting compounds such as InP. Its main feature is that, among all the compounds of the type $A^{III}B^{V}$, the enthalpy of formation of $B^{V}_{m}O_{n}$ (P_2O_5) is greater than that of $A^{III}_{2}O_3$ (In_2O_3) only for InP. Therefore, according to the results of thermodynamic analysis,[86] phosphorus should remove oxygen from indium, i.e. its transit reactions

$$0.3P_4O_{10}+2InP \rightleftharpoons In_2O_3+3.2P, \quad (14)$$

$$0.3P_4O_{10}+2In \rightleftharpoons In_2O_3+1.2P \quad (15)$$

will occur in the reverse direction—"reverse" transit.

However, it is believed[87] that the $InPO_4-P$, $In(PO_3)_3P$ pairs should be thermodynamically stable under equilibrium conditions in the In–P–O system. Thus in the above system the growing of regular films is possible only over an extremely long period as a result of the secondary interaction of the indium and phosphorus oxides with formation of $InPO_4$. Indeed, according to the literature data,[88,89] the composition of the intrinsic oxide layers on InP approaches that of $InPO_4$. Furthermore, in contrast to, for example, GaAs, non-oxidised indium has been detected in the intrinsic oxide films grown on InP.[90]

The thermo-oxidation of InP itself in the temperature range 575–675 °C is a two-stage process. The first stage ($n \simeq 0.5$) corresponds to diffusional control and the rate-limiting stage is apparently the diffusion of indium from the support. The second stage with n = 0.13 corresponds to the type of process in which the interaction in the solid phase, namely the formation of $InPO_4$, is determining. The process is limited by the mutual diffusion of the oxides. There is a high content of indium in the resulting layers (EAS, IRS), which indicates its presence in a free state. This may be a consequence of the degradation of the support[88] or, what is more likely, may be a result of reactions (14) and (15), which are apparently determining in the first stage. The $INPO_4$ content in the layers on the whole increases with increase in the process parameters, but the concentration of free indium also increases in the same direction (XSA, EAS). The latter is responsible for the very low resistivity of the films ($< 10^6$ Ω cm).

Thus the very mechanism of the formation of intrinsic dielectric layers on InP is responsible for their unsatisfactory properties and it is essential to introduce an impurity, in the first place with the aim of increasing the efficiency of the oxidation of indium both directly (with indium as the transit impurity) and indirectly by enhancing the oxidation of phosphorus (with phosphorus as the transit impurity) and of weakening its effects on In_2O_3 via reactions (14) and (15). Furthermore, in contrast to $Ga_2O_3-As_2O_5$ system, in the analogous $In_2O_3-P_2O_5$ system better possibilities arise for interactions, since indium possesses metallic properties to a greater extent than gallium, while phosphorus possesses non-metallic properties to a greater extent than arsenic. The correct choice of the impurity can therefore intensify the process, for example, by increasing the mutual diffusion on loosening.

The introduction of impurity compounds into the gas phase, capable of undergoing both the transit reactions indicated above and reactions responsible for the increase in the rate of diffusion ($PbCl_2$) or a possible catalytic effect (V_2O_5), does indeed increase the rate of formation of oxide layers on indium phosphide. Acceleration by a factor of 2–3 has been achieved as regards thickness and by a factor of 8–11 as regards time using $PbCl_2$; for V_2O_5, the above factors are 8–9 and 40–60 respectively. In both cases, the kinetics change compared with the impurity-free reference process. The introduction of $PbCl_2$ ensures a more favourable kinetic regime for film growth by increasing the amount of oxygen capable of being

"retained" in indium (EAS) and also by loosening the resulting layer by incorporating lead atoms in it. The films consist mainly of $InPO_4$; their composition also includes impurity components: lead and chlorine (XSA, EAS, IRS). Vanadium oxide is believed tentatively to accelerate the formation of films via a catalytic mechanism, but it is incorporated in the growing layer (IRS, XSA, EAS). The fraction of oxidised indium in these impurity layers is greater than in the reference layers, but the content of unoxidised indium is still appreciable and the dielectric characteristics are therefore unsatisfactory.

Good results are obtained by the preliminary deposition of a PbS layer on the InP surface to be oxidised. As in the oxidation of similar heterostructures based on silicon and gallium arsenide, in this case the process begins with the formation of a sulphate framework. Indium phosphate is then formed and adds to the framework. It may be that $PbSO_4$ phases interact with one another (IRS). In the vicinity of the outer interface of the heterostructure, mainly $PbSO_4$ is concentrated, the $InPO_4$ content increasing on moving towards the inner interface (IRS, EAS, XSA). Indium sulphides are formed at the inner interface (EAS), which diminishes sharply the concentration of indium in the films and frees them from the unoxidised indium. Therefore, in the oxidation of the InP/PbS structures, not only is the formation of the layers accelerated (by a factor of 4–6) but an appreciable increase in their electrical strength (approximately by an order of magnitude) compared with the reference standard is ensured.

Thus analysis of the surveyed data concerning the thermo-oxidation reactions of silicon and gallium arsenide in the presence of impurities shows that on silicon the greatest acceleration of the process is attained after the introduction of lead compounds, i.e. this element is optimal as a cation-forming agent. As mentioned above, among the anion-forming agents chlorine exerts the most favourable modifying effect on the properties of the layers, whilst oxygen compounds as a rule react too vigorously with the oxidisable surface.

The best cation-forming agent for gallium arsenide is antimony, which has the same valence as arsenic. Its compounds ensure an appreciable acceleration of the process. In addition, as already emphasised, here there is the greatest probability of the mutual dissolution of the intrinsic and impurity oxides, which promotes the healing of defects and the improvement of the properties of the resulting layers. Among anion-forming agents, sulphur is best. It binds the volatile components of the support and diminishes thereby the degradation of the inner interface, improving its properties. For compounds of the type $A^{III}B^{V}$ with a volatile component (B^{V}), the method of introduction of the impurity into the system which depends on the nature of the anion-forming element, i.e. the creation of a restricted impurity source, is convenient. Under these conditions, the deposited impurity layer not only interacts chemically with the support but also serves as a mechanical barrier to the evaporation of the volatile component.

In the thermo-oxidation of InP/PbS structures, the component A^{III} is bound chemically by sulphur on the inner interface which, together with the greater effectiveness of its oxidation as a result of the transit reaction, minimises the probability of the appearance of free indium in the resulting layers. In contrast to the corresponding structures based on gallium arsenide, the deposited impurity layer fulfills various functions in relation to the components of the support (A^{III} and B^{V}): it binds chemically the former, preventing its rapid diffusion into the film, and prevents the evaporation of the latter. The general criteria governing the selection of the impurity formulated above retain their validity also for a material such as indium phosphide which is not simple as regards the growing of dielectric layers.

References

1. V A Arslambekov, M Yu Potashnikov *Poverkhnost'. Fizika, Khimiya, Mekhanika*, 1987, (6) 104
2. T E Jackman, J R McDonald, L C Feldman, et al. *Surf. Sci.*, 1980, **100**(1) 35
3. B E Deal, A S Grove *J. Appl. Phys.*, 1965, **36**(12) 3770
4. F A Irene *J. Appl. Phys.*, 1983, **54**(9) 5416
5. J Blank *Appl. Phys. Lett.*, 1978, **33**(5) 424
6. G Camera Roda, F Santarelli, G C Sarti *J. Electrochem. Soc.*, 1985, **132**(8) 1903
7. Yu-Leng Lu, Y C Cheng *Acta Phys. Sin.*, 1985, **34**(4) 447
8. A Lora-Tamajo, E Dominques, E Lora-Tamajo *Appl. Phys.*, 1978, **17**(1) 79
9. N A Kolobov, M M Samokhvalov *Diffuziya i Okislenie Poluprovodnikov* (Diffusion and Oxidation of Semiconductors), Metallurgiya, Moscow, 1975, 452 pp
10. W A Tiller *J. Electrochem. Soc.*, 1980, **127**(3) 619
11. W A Tiller *J. Electrochem. Soc.*, 1980, **127**(3) 625
12. W A Tiller *J. Electrochem. Soc.*, 1981, **128**(3) 689
13. W A Tiller *J. Electrochem. Soc.*, 1983, **130**(2) 501
14. Ya A Ugai, V Z Anokhin, I Ya Mittova, et al. *Dokl. Akad. Nauk SSSR*, 1981, **259**(3) 648
15. Ya A Ugai, A M Khoviv, V Z Anokhin, et al. *Dokl. Akad. Nauk SSSR*, 1982, **267**(1) 144
16. Ya A Ugai, V Z Anokhin, A M Khoviv, I Ya Mittova, et al. *Dokl. Akad. Nauk SSSR*, 1982, **266**(5) 1188
17. B E Deal, M Sklar *J. Electrochem. Soc.*, 1965, **112**(4) 430
18. R M Burger, R B Donovan (Editors) *Fundamentals of Silicon Integrated Device Technology* (Translated into Russian), Mir, Moscow, 1969, 451 pp
19. Ya A Ugai, T A Gadebskaya, V Z Anokhin, et al. *Zh. Fiz. Khim.*, 1979, **53**(8) 2012 [English translation in *Russ. J. Phys. Chem.*, 1979(8)]
20. Ya A Ugai, T A Gadebskaya, I Ya Mittova *Zh. Fiz. Khim.*, 1980, **54**(6) 1548 [English translation in *Russ. J. Phys. Chem.*, 1980(6)]
21. Ya A Ugai, V Z Anokhin, V A Lobova, et al. *Zh. Fiz. Khim.*, 1981, **55**(7) 1873 [English translation in *Russ. J. Phys. Chem.*, 1981(7)]
22. Ya A Ugai, I Ya Mittova, V Z Anokhin, et al. *Zh. Fiz. Khim.*, 1982, **57**(3) 619 [English translation in *Russ. J. Phys. Chem.*, 1982(3)]
23. Ya A Ugai, I Ya Mittova, V Z Anokhin, et al. *Zh. Fiz. Khim.*, 1982, **56**(8) 1917 [English translation in *Russ. J. Phys. Chem.*, 1982(8)]
24. Ya A Ugai, I Ya Mittova, V A Lobova, et al. *Zh. Fiz. Khim.*, 1982, **56**(3) 614 [English translation in *Russ. J. Phys. Chem.*, 1982(3)]
25. Ya A Ugai, I Ya Mittova, V I Emel'yanenko, et al. *Zh. Fiz. Khim.*, 1983, **57**(10) 2491 [English translation in *Russ. J. Phys. Chem.*, 1983(10)]
26. Ya A Ugai, I Ya Mittova, V I Emel'yanenko, et al. *Zh. Fiz. Khim.*, 1984, **58**(3) 588 [English translation in *Russ. J. Phys. Chem.*, 1984(3)]

27. I Ya Mittova, S I Emel'yanenko, N M Medvedev *Zh. Fiz. Khim.*, 1985, **59**(7) 1604 [English translation in *Russ. J. Phys. Chem.*, 1985(7)]
28. I Ya Mittova, G A Lapina, N M Medvedev *Zh. Fiz. Khim.*, 1985, **59**(8) 1884 [English translation in *Russ. J. Phys. Chem.*, 1985(8)]
29. I Ya Mittova, B V Borzakova, N M Medvedev *Zh. Fiz. Khim.*, 1986, **60**(7) 1607 [English translation in *Russ. J. Phys. Chem.*, 1986(7)]
30. Ya A Ugai, V Z Anokhin, I Ya Mittov, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1974, **10**(4) 726
31. I Ya Mittova, V V Pukhova, V R Pshestanchik *Dokl. Akad. Nauk SSSR*, 1987, **295**(1) 112
32. Ya A Ugai, V Z Anokhin, I Ya Mittova *Elektron. Tekhnika. Materialy*, 1984, (9) 33
33. E S Vorontsov, V M Strukov *Kinet. Katal.*, 1975, **16**(4) 1075
34. V M Strukov, E S Vorontsov *Kinet. Katal.*, 1976, **17**(6) 1606
35. Ya A Ugai, V Z Anokhin, I Ya Mittova, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1975, **11**(4) 592
36. I Ya Mittova *Fizikokhimiya Termicheskogo Okisleniya Kremniya v Prisutstvii Primesei* (Physical Chemistry of the Thermooxidation of Silicon in the Presence of Impurities), Izd. Voronezh. Gos. Univ., Voronezh, 1987, 103 pp
37. I Ya Mittova, V Z Anokhin, V A Lobova *Poluprovodnikovye Materialy i Ikh Primenenie* (Semiconducting Materials and Their Applications), Izd. Voronezh. Gos. Univ., Voronezh, 1977, p. 36
38. I K Marshakov, Ya A Ugai, V Z Anokhin, I Ya Mittova, et al. *Kinetika i Mekhanizm Termicheskikh Reaktsii v Tverdom Tele: Tezisy Dokladov 4 Vsesoyuznogo Soveshchaniya, Minsk* (Kinetics and Mechanism of Thermal Reactions in the Solid State: Abstracts of Reports at the 4th All-Union Conference, Minsk), Minsk, 1975, p. 113
39. I K Marshakov, V Z Anokhin, I Ya Mittova, et al. *Zh. Fiz. Khim.*, 1976, **50**(12) 3094 [English translation in *Russ. J. Phys. Chem.*, 1976(12)]
40. I K Marshakov, V Z Anokhin, V A Lobova, et al. *Kinetics of the Growth of Bismuth Silicate Films on Silicon*, Voronezh State University, Voronezh, 1977, 6 pp. Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 20.02.1978, No. 3416-77
41. I Ya Mittova, V R Pshestanchik *X Vsesoyuznoe Soveshchanie po Kinetike i Mekhanizmu Reaktsii v Tverdom Tele: Tezisy Dokladov, Chernogolovka* (The Xth All-Union Conference on the Kinetics and Mechanism of Solid State Reactions: Abstracts of Reports, Chernogolovka), Chernogolovka, 1989, Vol. 1, p. 28
42. V V Arslambekov *Mekhanizm Vzaimodeistviya Metallov s Gazami* (The Mechanism of the Interaction of Metals with Gases), Nauka, Moscow, 1964, p. 86
43. I Ya Mittova, V V Pukhova, T I Samylina *Zh. Fiz. Khim.*, 1985, **59**(10) 2421 [English translation in *Russ. J. Phys. Chem.*, 1985(10)]
44. I Ya Mittova, V V Pukhova, V N Semenov *Zh. Fiz. Khim.*, 1986, **60**(1) 50 [English translation in *Russ. J. Phys. Chem.*, 1986(1)]
45. Ya A Ugai, I Ya Mittova, V V Pukhova, et al. *Zh. Fiz. Khim.*, 1982, **56**(11) 2707 [English translation in *Russ. J. Phys. Chem.*, 1982(11)]
46. Ya A Ugai, I Ya Mittova, V V Pukhova, et al. *Zh. Fiz. Khim.*, 1984, **58**(2) 315 [English translation in *Russ. J. Phys. Chem.*, 1984(2)]
47. Ya A Ugai, I Ya Mittova, V V Pukhova, et al. *Zh. Fiz. Khim.*, 1983, **57**(9) 2186 [English translation in *Russ. J. Phys. Chem.*, 1983(9)]
48. R J Kriegler, J C Cheng, D R Colton *J. Electrochem. Soc.*, 1972, **119**(3) 388
49. R J Kriegler *Thin Solid Films*, 1972, **13**(1) 11
50. C M Osburn *J. Electrochem. Soc.*, 1983, **121**(6) 809
51. M Hamasaki, *J. Appl. Phys.*, 1981, **52**(5) 3484
52. G Shiraki *Jpn. J. Appl. Phys.*, 1975, **14**(6) 747
53. Ya A Ugai, I Ya Mittova, N I Ponomareva, et al. *Zh. Fiz. Khim.*, 1982, **56**(7) 1610 [English translation in *Russ. J. Phys. Chem.*, 1982(7)]
54. Ya A Ugai, I Ya Mittova, V Z Anokhin *Zh. Fiz. Khim.*, 1983, **57**(1) 79 [English translation in *Russ. J. Phys. Chem.*, 1983(1)]
55. V Z Anokhin, I Ya Mittova, N I Ponomareva, et al. *Zh. Fiz. Khim.*, 1981, **55**(11) 2765 [English translation in *Russ. J. Phys. Chem.*, 1981(11)]
56. E P Domashevskaya, I Ya Mittova, N I Ponomareva, et al. *Poverkhnost'. Fizika, Khimiya, Mekhanika*, 1985, (6) 138
57. Ya A Ugai, I Ya Mittova, V Z Anokhin *Zh. Fiz. Khim.*, 1981, **55**(10) 2672 [English translation in *Russ. J. Phys. Chem.*, 1981(10)]
58. Ya A Ugai, V Z Anokhin, I Ya Mittova, et al. *Zh. Fiz. Khim.*, 1980, **54**(5) 1133 [English translation in *Russ. J. Phys. Chem.*, 1980(5)]
59. Ya A Ugai, V Z Anokhin, I Ya Mittova, et al. *Zh. Fiz. Khim.*, 1981, **55**(4) 946 [English translation in *Russ. J. Phys. Chem.*, 1981(4)]
60. R L Meck *J. Electrochem. Soc.*, 1973, **120**(2) 308
61. I Ya Mittova, V R Pshestanchik *Termodinamika i Materialovedenie Poluprovodnikov: Tezisy Dokladov III Vsesoyuznoi Konferentsii, Moskva* (Thermodynamics and Materials Science of Semiconductors: Abstracts of Reports at the IIIrd All-Union Conference, Moscow), Moscow, 1986, Vol. 2, p. 26
62. C D Thurmond, G P Schwartz, G W Kammlott, et al. *J. Electrochem. Soc.*, 1980, **127**(6) 1366
63. P W Lander, F L Schuermeyer, R L Johnson, et al. *J. Vac. Sci. Technol.*, 1980, **17**(5) 964
64. F J Grunthaner, P J Grunthaner, R P Vasquez, et al. *J. Vac. Sci. Technol.*, 1979, **16**(5) 1443
65. Wang Hun, A Reyes-Mena, D Lichtman *J. Electrochem. Soc.*, 1982, **129**(4) 851
66. P N Butcher, B J Sealy *Electron. Lett.*, 1977, **13**(19) 558
67. I Ya Mittova, G V Borzakova, N M Medvedev, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1989, **25**(6) 912
68. C W Wilmsen *Thin Solid Films*, 1976, **30**(1) 105
69. I Ya Mittova, V V Sviridova, V N Semenov, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1989, **25**(6) 908
70. I Ya Mittova, V V Vasil'eva, V N Semenov, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1988, **24**(4) 538
71. I Ya Mittova, V V Vasil'eva, V A Terekhov, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1988, **24**(12) 1941
72. I V Tananaev, M Ya Shpirt *Khimiya Germaniya* (The Chemistry of Germanium), Khimiya, Moscow, 1967, 454 pp

73. E K Kazenas, D M Chizhikov *Davlenie i Sostav Para nad Okislami Khimicheskikh Elementov* (The Pressure and Composition of the Vapour Over the Oxides of Chemical Elements), Nauka, Moscow, 1976, 342 pp
74. I Ya Mittova, V V Sviridova, I A Kolyukaeva, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1989, **25**(12) 1954
75. I Ya Mittova, G V Borzakova, V V Sviridova, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1989, **25**(8) 1244
76. I Ya Mittova, V V Pukhova *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1986, **22**(6) 885
77. I Ya Mittova, V V Pukhova, V A Terekhov, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1988, **24**(10) 1592
78. I Ya Mittova, V V Pukhova, V N Semenov, et al. *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1987, **23**(5) 717
79. I Ya Mittova, V V Pukhova, L Zh Noniashvili *Elektron. Tekhnika. Materialy*, 1987, **2**(223) 60
80. I Ya Mittova, V V Pukhova, I F Klement'eva *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1988, **24**(9) 1431
81. I Ya Mittova, V I Chavkina, V N Semenov *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1987, **23**(7) 1212
82. I Ya Mittova, V I Chavkina, V N Semenov *Izv. Akad. Nauk SSSR, Neorg. Materialy*, 1986, **22**(6) 893
83. I Ya Mittova, N I Ponomareva, M N Kuznetsova *Zh. Fiz. Khim.*, 1985, **59**(3) 758 [English translation in *Russ. J. Phys. Chem.*, 1985(3)]
84. G A Razuvaev, B G Gribov, G A Domrachev, B A Salamatin *Metalloorganicheskie Soedineniya v Elektronike* (Organometallic Compounds in Electronics), Nauka, Moscow, 1972, 479 pp
85. I Ya Mittova, N I Ponomareva *Zh. Fiz. Khim.*, 1985, **59**(9) 2331 [English translation in *Russ. J. Phys. Chem.*, 1985(9)]
86. I Ya Mittova, V R Pshestanchik, V V Sviridova *Termodinamika i Materialovedenie Poluprovodnikov; Tezisy Dokladov IV Vsesoyuznoi Konferentsii, Moskva* (Thermodynamics and Materials Science of Semiconductors: Abstracts of Reports at the IVth All-Union Conference, Moscow), Moscow, 1989, Part 1, p. 95
87. G P Schwartz, W A Sunder, J E Griffiths *J. Electrochem. Soc.*, 1982, **129**(6) 1361
88. J E Griffiths, G P Schwartz, W A Sunder, H Schonhorn *J. Appl. Phys.*, 1982, **53**(3) 1832
89. G Hollinger, E Bergignat, J Joseph, Y Robach *J. Vac. Sci. Technol.*, 1985, **A3** 2082
90. E Yamaguchi, K Ando *J. Appl. Phys.*, 1980, **51**(9) 5007