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Thin Solid Films 367 (2000) 75–84

thin solid films

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Molecular beam epitaxy of silicon–germanium nanostructures

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Abstract

The current status of the research in the field of synthesis and application of silicon and germanium-based nanostructures formed by the process of 3D island self-organization is reviewed in the present paper. There was an obvious conclusion that elastic deformations in epitaxial films and 3D islands are the key factor which is not only the reason of the transition from planar to Stranski–Krastanow mechanism of growth, but also influences the next stages of islands evolution including their shape, size and spatial distributions. There are many cases when this factor makes crucial changes to the classical set of phase-formation mechanisms right up to an equilibrium coexistence of islands on a surface. Various types of ordering were classified in the nanocluster systems under consideration: in cluster shape, in its size, in the distance between nearest islands, as well as ordering through vertical, i.e. in successively growing multilayer structures containing quantum dots. The results of recent original investigations of electrical and optical properties of self-assembled arrays of Ge quantum dots are presented.

Keywords: Molecular beam epitaxy; Germanium; Silicon; Heteroepitaxy; Quantum dots; Self-organization in epitaxy

1. Introduction

Germanium-on-silicon nanostructures are of great technological interest provoked by impressing progress in the field of development of promising devices using quantum effects. Innovative light-emitting and optoelectronic devices make it possible for the silicon-based technology to be quite competitive with such traditional optoelectronic materials as III-V compounds [1–5]. Until recently, this has been rather exotic field of research, but many experts believe that a real revolution may happen to the silicon-based technology. Most of the known technological centers, among which are IBM, NEC, Daimler-Benz, Toshiba, Mitsubishi, etc., extend their studies aimed at the use of Ge–Si heterosystems for designing microwave devices and optoelectronic units [1,5]. Development of high-resolution techniques, such as STM and AFM, enabled scientists to expand fundamental knowledge on the surface processes at early stages of heteroepitaxy. These studies are also of great practical importance to researchers who work on improvement of methods for molecular beam epitaxy (MBE) of nanostructures based on Si–Ge heterosystems.

The growing interest in studies of semiconductor nanostructures gave rise to a consistent increase in the number of publications in the field. Fig. 1 is a histogram of the annual number of scientific publications dealing with 'quantum dots'. A steady increase in the number of publications is seen to argue the ever-growing interest to the problem. There was no change in the technology for fabrication of quantum dot (QD) structures until 1992. Before that time, photolithography was the basic method for fabricating these structures that imposed restrictions on the minimal size. The discovered effect of self-organization of ordered arrays of nanosize islands in Ge–Si and InAs–GaAs heterosystems allowed for ultrasmall defect-free QDs to be obtained at the density of 10^{10}–10^{11} cm^{-2} and resulted in more distinct atomic-like characteristics observed in the pertinent electron and optical spectra. The progress in this field is illustrated in Fig. 2 where the number of publications devoted to Ge–Si heterosystems with QDs is plotted vs. years. The authors of [6–8] were first to suggest in 1993–1994 the use of island arrays as QDs in the InAs-GaAs system. However, our paper [9], published as early as 1992, mentioned the use of Ge islands as QDs while observing the effects of resonance tunneling and Coulomb blockage. That was, seemingly, the pioneering publication in the field. The transition from the 2D film growth to nucleation of 3D islands (the Stranski–Krastanow mechanism) has long been under study with germanium on silicon heterosystem as an example. For the Ge–Si heterosystems, the study accomplished in

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PII: S0040-6090(00)00667-2

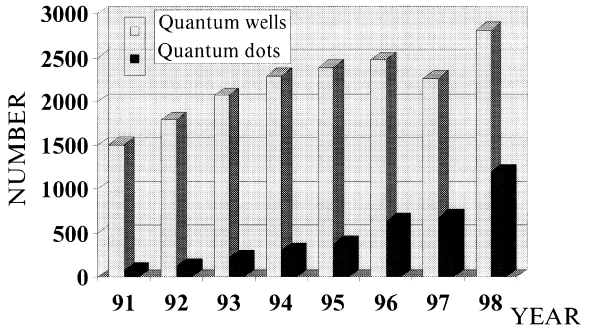

Fig. 1. The number of publications per year by Materials Science Citation Index (MSCI) for the years 1990–1998. The selection by keywords 'quantum wells' and 'quantum dots'.

the Institute of Semiconductor Physics as early as 1974 [10] was, probably, the first time when formation of pseudomorphic germanium bands (now referred as quantum wires) replicating the step share and of nanosize islands (now QDs) were observed. Kinetic diagrams of structural transformation based on experimental data were obtained by us in Ref. [11]. The diagrams show ranges of occurrence of films (stressed and plastically deformed continuous and island-like ones) in the space of basic MBE parameters. The formations of islands with misfit dislocations (MD) during Ge–Si growth (as well as during InAs–GaAs growth) is undesirable because hinders the growth of perfect films. However, these islands, unless the process is brought to introduction of dislocations into them, can be used for studying quantum phenomena in solids. There are no MDs in these islands at relatively low temperatures, even if their thickness exceeds considerably the critical value. The most spectacular data were presented by Eaglesham and Cerullo for Ge–Si [12] and by Guha et al. for InGaAs–GaAs [13]. There are the publications which launched intensive studies of the self-organization phenomenon as that of practical importance to nanoelectronics.

The aim of the present work is to analyze the progress and

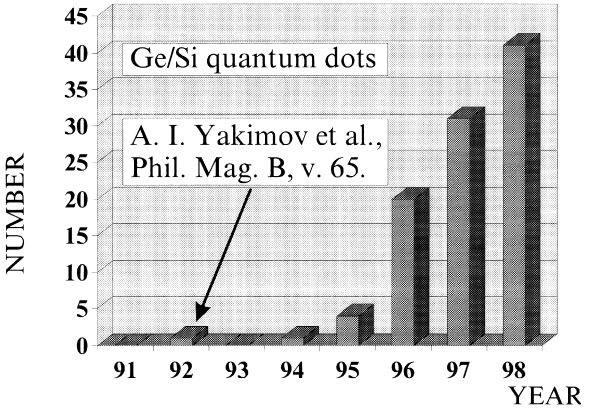

Fig. 2. The subsample from the 'quantum dots' body of data: papers in which an islanding of Ge(GeSi) on Si is investigated, as well as features of these objects.

current status in the field of the self-organization mechanisms of QD ensembles during heteroepitaxy. A number of review papers [14–16] have already dealt with this problem. We are not aspire to completeness but try to discuss the commonly accepted concepts of the self-organization mechanisms and to expand them with the data based on our experimental results on synthesis of Ge–Si heterosystem comprising QDs and characterization of their electron and optical properties.

Section 2 is devoted to driving forces and principal mechanisms of the evolution and ordering of nanoobjects in heterosystems with great misfit of lattice constants during MBE and heat treatment.

Experimental observations of cluster formation and self-organization of GeSi nanostructures on the Si surface are discussed in Section 3. The results of our studies on electron and optical properties of heterostructures and multilayer compositions comprising QDs are presented in Section 4.

2. Fundamentals

Stages of nucleation and islands growth can be identified during the formation process of 3D islands. Principal features of the island nucleation in epitaxial heterosystems are governed by the competition between the surface energies of the deposit and the substrate, as well as the energy of the film-substrate interface and internal energy of the island's bulk. The total free energy of a new nucleus on the substrate surface is [17]

$$\Delta G = -V\Delta\mu + \gamma s + E_i(V, h/l) \quad (1)$$

Here, the first term is the chemical work to form of island of volume V, $\Delta\mu$ is the thermodynamic driving force of crystallization–supersaturation; the second term is the additional energy of an extra surface s, γ is the surface energy of the nucleus. The first and the second terms are the classical version of the nucleation theory (see e.g. [18]), while the last term is only included for the case of nucleating stressed deposits. When misfits are so large as those in the Ge–Si system, the magnitude of this additional energy depends not only on the nucleus volume but also on the shape; h/l is the aspect ratio of the nucleus height to its lateral size. The last term of the equation, the contribution of which depends on h/l, is of considerable importance in the 2D–3D transition. This contribution, after Muller and Kern [17], looks like a rapidly decreasing function of aspect ratio. The more pronounced three-dimensional character of the nucleus is, the less is the extra contribution of stress energy to the total free energy. The surface energy of the Ge wetting layer surrounding the Ge 3D nucleus depends on the thickness of Ge layer too [19].

Thus, a decrease in the stress energy at the top of islands due to elastic relaxation is the key factor for transition from 2D layer to 3D-island growth of pseudomorphic films and the misfit stresses become of critical importance. (For the

case of homoepitaxy, 3D islands are not nucleated at a sufficiently pure surface of almost all semiconductors and the films are grown through either steps motion or nucleation and coalescence of 2D islands (2D growth).) It will be shown below that stresses are also of considerable importance in evolution of 3D islands and their size distribution.

Asaro and Tiller [20] (1972) and Grinfeld [21] (1986) have demonstrated the critical role of the elastic relaxation of strains resulting in morphological instability of film surface. The underlying concept of this model is that the rough surface of a stressed layer possesses a lower total energy due to the elastic strain relaxation at the tops of ridges. An increase in the surface energy is the factor counteracting the development of the film relief but decreases only partly the energetic profit due to relaxation. The more is the misfit between lattice constants of the film and of the substrate, the lower is the thickness at which the pseudomorphic film loses its morphological stability. Nucleation of 3D islands is the extreme case of morphological instability of stressed films, such a phenomenon is observed for systems with considerable misfit of lattice constants of the film and substrate. Among such systems are Ge–Si and InAs–GaAs. If the surface energy of the new phase could be diminished, the stressed film loses its morphological stability at smaller misfits. For example, when a stressed film contacts a liquid phase, i.e. the film surface energy is considerably lower of the surface energy of the film-vacuum (or vapor) interface, nucleation of islands is observed in the system Ge_xSi_{1-x}/Si(001) at very small misfits: $x \sim 0.05$ ($\varepsilon \sim 0.2\%$) [22]. Again, similarly low magnitudes of elastic deformations gave rise to ramification of the island shape in the system $In_xGa_{1-x}As$/GaAs(111)A which was also synthesized by contacting with liquid phase [23]. (This is the only example of formation of dislocation-free islands on (111)A substrate, which thicknesses are exceeding the critical value for MDs introduction. This result seems to be a consequence of a decrease in the surface energy of the film in contact with the liquid phase.)

In terms of the classical concept [24], the process of formation of a new phase involves basic stage of nucleation, independent growth of the nuclei and, finally, evolution of the nuclei in cooperation with one another, the so-called Ostwald ripening (OR). Latter phenomenon is the latest growth stage of grains (nuclei) of a new phase in time. The earliest comprehensive OR theory was developed by Lifshitz and Slyozov for the case of grain formation through the bulk of supersaturated solid solution [25] and modified for surface by Chakraverty [26]. This theory is currently used for interpreting processes observed on semiconductor surfaces by means of up-to-date high-resolution techniques (e.g. [27–31]). According to this model, the latest stage of cluster growth (ripening) is determined by the Gibbs-Thompson interaction of nuclei, arranged inside a supersaturated 'sea' of adatoms (equilibrium vapor pressure must be higher over a curved surface. Large islands grow at the expense of small ones). Diffusion and incorporation of adatoms are limiting factors of the OR process, they affect the shape of the function of the island size distribution [28]. Another important features of the OR process are a continuous increase of the average island size and broadening of the non-normalized island size distribution with time.

Experimental observations of the evolution of 2D silicon islands on Si(001) surface are in good agreement with the OR model (see e.g. [28]). Fig. 3 shows a schematic of nucleation and evolution of an epitaxial layer in terms of three stages of the classical model [24]. At the starting point (position (a)) the substrate surface is covered by a supersaturated adsorbate. The first stage is the nucleation of 2D islands (position (b)). The next stage is island's growth (position (c)) when the supersaturation is lowered around the islands but the latter do not as yet interact. Therefore, nucleation continues at the sites away from already formed islands. After the areas of diffusive 'nutrition' of the islands have been overlapped (position (d)) and the supersaturation level falls down at between the islands, the probability of new nucleation decreases, and the third stage starts. This is the stage of correlated growth of islands, or Ostwald ripening. Large islands grow and small islands disappear (position (e)). This stage can take long time if the system is closed and the amount of adatoms is less then one monolayer [28]. The size distribution of islands is a reproducible function which essentially depends on the substrate orientation (see e.g. [32]). In the case of uninterrupted feeding of adatoms to the surface (open system) the islands extend to join one another, and a new continuous monolayer is formed (position (f)). If the study is aimed at synthesis of an island

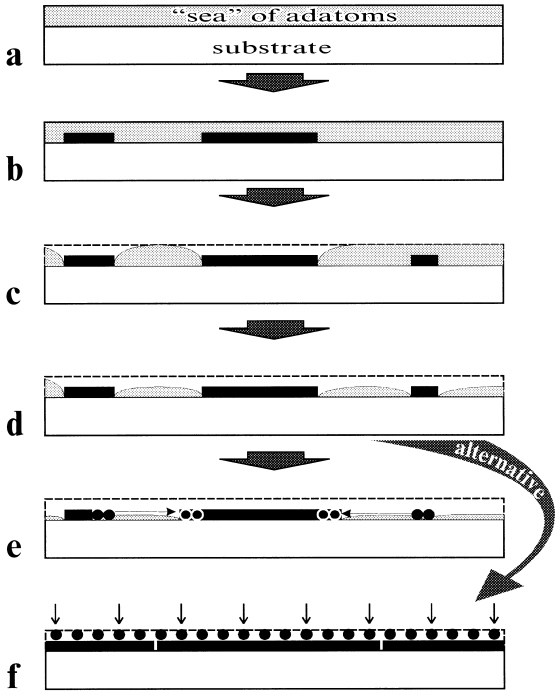

Fig. 3. Schematic stages of formation of a new ML in classic representation from Kukushkin and Osipov [24] applied to MBE (Si on Si, for example).

film, then the OR stage can be of primary importance and determines the shape of island size distribution. Much attention is paid in the literature to applicability of the OR mechanism to this case.

Among the statements of the fundamental work [25] on grain ripening by Lifshitz and Slyozov is that elastic deformations in grains may be taken into account but not have essential impact upon the shape of the final distribution because these deformations are a second-order factor. Indeed, for the three-dimensional case under consideration by Lifshitz and Slyozov, stresses in 3D grains of a new material may be treated as an extra portion of the free energy of the cluster which influences the rate of the cluster nucleation and growth. Drucker [33] used such an approach for computing OR evolution of 2D islands on the substrate surface. However, recent studies have demonstrated that elastic deformations in epitaxial films and emerging 3D islands are the key, more complex, factor. There are many cases when this factor makes dramatic changes to the classical set of phase-formation mechanisms. For example, for the case of Ge-on-Si and InAs-on-GaAs, the occurrence of these deformations leads to transition from the layer-by-layer growth to nucleation of 3D clusters at the surface of the underlying Ge (or InAs) layer, i.e. achievement of the Stranski–Krastanow mechanism. Remarkably non-uniform elastic relaxation of the islands along their height causes shape-dependent elastic relaxation (i.e. energetic profit). As a result, several discrete cluster shapes ('hut', 'dome', 'superdome') appear which are the most energetically favorable. Elastic deformations at the cluster base and in the adjacent substrate region increase as the cluster increases in size. As a result, the growth rate of an island decreases with its size [34–36]. This rising attachment barrier is treated as one of the principal reasons for narrowing the island size distribution against that predicted by the OR theory (see e.g. [35]). The elastic deformations and their relaxation in islands can under certain conditions predominate until a quasiequilibrium state is established. In this case the ensemble of clusters is time-independent in both island shapes and their size distribution and, hence, does not obey the laws of the OR model [31,37–42].

Fig. 4 summarizes schematically the main stages of 3D formation in Ge–Si system and their distinctions from the classical model. Similar to Fig. 3, the initial state (a) is the supersaturated adsorbate of adatoms but they are now on the surface of the underlying layer of a deposited material (wetting layer). Nucleation of 3D 'hut'-clusters (position (b)) is accounted for by relaxation of the elastic deformations as it was discussed earlier (the first distinctive feature against the classical version). Then the clusters of two different shapes, 'hut' and 'dome', appear (position (c)). Energetic profitability of the first and the second shapes depends on their volume but they can coexist [38,39] (the second distinctive feature). Atoms can transfer to a more energetically favorable shape 'dome' (position (d)), and one can say that the OR mechanism became operative [43].

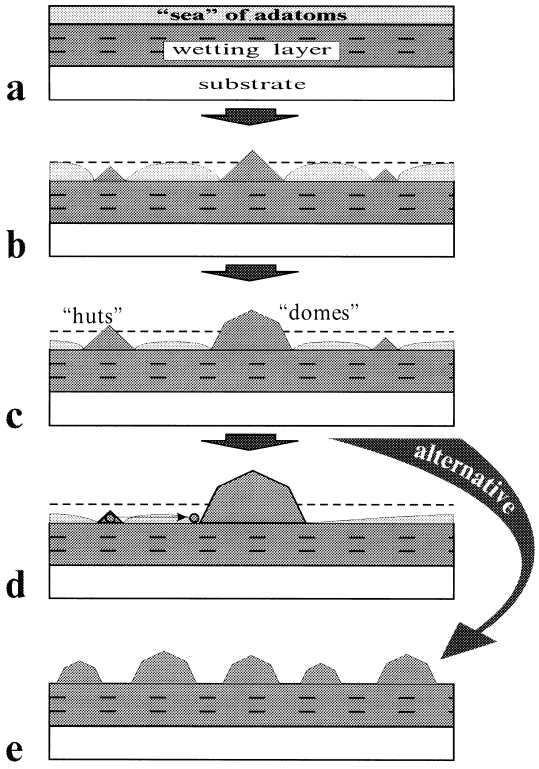

Fig. 4. Schematic stages of a 3D formation in the Ge/Si (001) system.

However, there is no continuous size distribution but a bimodal distribution [38,43]. A reverse transfer from 'dome' to 'hut' was even observed [40] (the third distinctive feature). A quasiequilibrium state of the system may occur when practically no change in time happen to the cluster size and shape in the absence of a flux from outside [41] (position (e), the fourth distinctive feature). Cluster interaction through overlapped fields of elastic deformations in the substrate was theoretically substantiated to occur under certain conditions [44,45]. For this reason, the spatial ordering of island distribution can be improved (the fifth distinctive feature).

3. Growth and particular features of self-ordering of Ge nanocluster ensembles

3.1. Morphological reconstructions

Several stages of island evolution were experimentally observed in Ge–Si heterosystems during an increase in the film effective thickness. These stages are different for [001] and [111] directions of growth. In terms of generation of quantum-size objects, the (001) surface is unique: this is the only surface where compact dislocation-free 3D islands of 10–100 nm were discovered (Fig. 5). These islands appear upon formation of a continuous Ge film (wetting layer), domains of which are easily observable between islands in Fig. 5. The start of 3D cluster nucleation is accompanied by

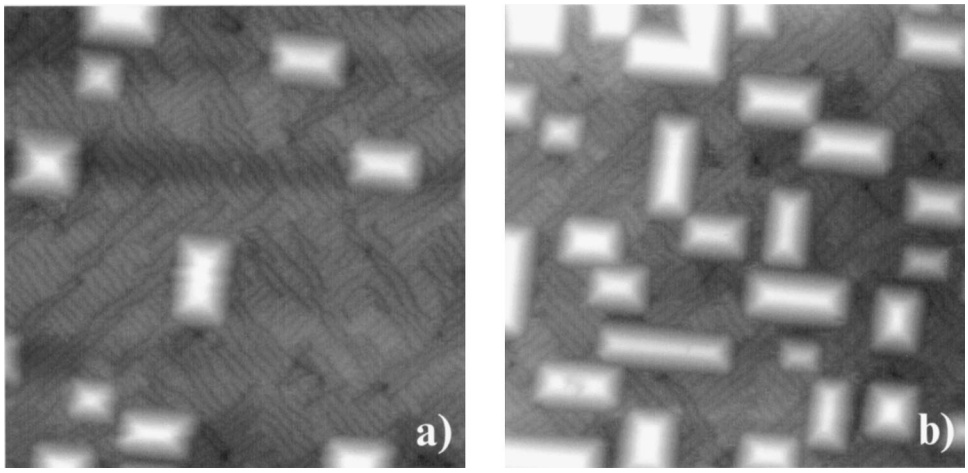

Fig. 5. STM sample images of the Ge 'hut'-cluster growth on (001) surfaces of Si as functions of coverage: (a) d_{eff} of Ge = 4.6 ML, and (b) d_{eff} of Ge = 8 ML. Image area: 160 × 160 nm. Growth temperature is 300°C, growth rate is 1 ML/200 s.

appearance of strikes in the RHEED patterns, which are assigned to electron scattering at {105} planes. These islands were called 'hut'-clusters [46] due to their shape. As the average film thickness increases, RHEED patterns start showing {113} and {102} planes along with {105}. (Notice that the first research on RHEED detection of exactly these planes of Ge islands on Si(001) surface was accomplished in the Institute of Semiconductor Physics, Novosibirsk, Russia as early as 1987 [47].) This stage is referred to as formation of 'dome'-clusters. On passing from 'hut'-clusters (15–20 nm in basis size) to 'dome'-clusters (50–100 nm in average size), the relaxation level of mechanical stresses increases. After Floro et al. [48], the material is elastically relaxed by 20% in 'hut'-clusters but by more than 50% in 'dome'-islands because of their higher aspect ratio. In the latter case the islands keep on coherency with the substrate. From numerous experimental observations, the last stage of morphological and structural evolution of Ge islands on Si(001) and Si(111) is formation and rapid growth of plastically deformed 3D islands with MDs at the island-substrate interface [11]. We showed earlier [49] that heterosystems with islands of required shape and size can be intentionally synthesized by controlling the growth process using in situ dynamic RHEED technique. In this case an increase in the surface supersaturation results in shortening the migration length of atoms to be incorporated and, as a consequence, in an increase in the number of nucleation sites. Thus, the island density increases at a simultaneous decrease in their size.

3.2. Self-organization effects

The array ordering process gives rise to an appearance of islands with preferable characteristics, such as size, shape, nearest neighbor distance and their mutual arrangement. This is the result of minimization of the total free energy in the system. The occurrence of the preferable characteristics must be observed in the spectra of electron scattering, electron and X-ray diffraction upon their interaction with the surface containing nanostructures, as well as in electron and optical spectra. Considerable attention was given in the literature to the size distribution of Ge islands since this parameter of a QD system is of great practical importance. Characteristic island size distributions and the range of normalized standard deviations to characterize distribution broadening are given in Ref. [31]; they are 0.5–0.9 for 'hut'-clusters and 0.1–0.3 for 'dome'-islands. (In this work the Ge layers were grown by chemical vapor deposition in H_2 ambient.) The more narrow distributions for 'dome'-clusters are accounted for by the fact that the increased elastic deformation in the substrate and cluster bottom at an increase in the cluster size is considered among the main reasons for decelerating the cluster growth rate (in contrast to the island evolution according to OR mechanism). A similar regularity was established for 'hut'-clusters synthesized at direct evaporation of Ge [36]: nonlinear increase in the cluster size with the increase of the effective thickness of Ge film is seen in Fig. 5, and the growth rate decreases when the Ge islands grow larger. This effect is studied in more detail in Ref. [36]. The result is a remarkable narrowing of the island size distribution [35]. That was exactly the effect of narrowing the size distribution which attracted much attention to these objects and determined alternative names of the process: self-assembling, self-organizing (Leonard et al. [6,7] were the first who used these names). The most uniform size distribution of Ge islands was reported in Ref. [50] (normalized standard deviation is 0.032). The authors assert that such a narrow distribution was obtained due to a very careful choice of island growth.

There may be distinguished the following alternatives, among the others referred to in the literature, for obtaining

islands more uniform in size: (a) application of misoriented substrates and (b) the use of a special method to achieve simultaneous nucleation of clusters [51]. The following facts of common knowledge and speculations can support these alternatives. Goldfarb et al. [29] demonstrate the details of transition from 2D to 3D growth and earliest stages of formation of 'hut'-clusters. 3D islands appear in noticeably different moments of time, they are nucleated at faults of the upper 2D layer that supports experimentally the general opinion on the determinative role of the factor of heterogeneous cluster nucleation. Ordering of steps at the planes misoriented from (001) is widely used for generating QD arrays in the InAs-GaAs system (see e.g. one of the last papers by Kim et al. [52] and references therein). Such an approach is less used to growth of Ge islands, although there is a spectacular work [53] reporting synthesis of Ge islands with better than 10% uniform distribution along both height and surface area. To improve step ordering at the 2D growth stage, the authors not only employed specific features of step formation at misoriented substrates but also enhance the 2D ordering by means of pre-growing a multilayer stressed superlattice of GeSi–Si.

The simultaneous nucleation of islands throughout the substrate surface can be provided through momentary increase of germanium flux at the early stage of the nanostructure growth. We discovered the synchronizing effect of periodical short-term variations in the surface supersaturation on the 2D nucleation earlier, while studying homoepitaxy of Ge and Si. Based on this effect, we substantiated and achieved the synchronized nucleation MBE method [51]. Later, an optimized method for synthesis of such quantum structures as vertical superlattices, quantum wires or QDs at cyclic supersaturation for growing each atomic layer constituting the film was proposed and developed [54].

Spatial clusters ordering is the weakest kind of ordering due to a weak interaction between the islands at the earliest stage of their growth. Therefore, pre-generation of ordered sites for nanocluster nucleation is the most attractive way to achieve their later spatially ordered state. The successive growth of layers with Ge islands to be covered by the material matching the substrate (Si) was shown [15] to enhance island ordering in both their size and surface area. Cluster-induced disturbance of elastic deformation fields penetrates for various distances into the covering layer depending on the volume of an individual island and on island agglomeration. Sites for preferable nucleation of new islands at the next 'floor' are formed at the surface of the covering layer. Control of the thickness of the covering layer makes it possible to minimize the effect of 'weak' islands. Both theoretical and experimental studies in the field were accomplished; several identical examples can be given for systems III–V [16] and Ge–Si [15,55]. These multilayer heterostructures with QDs are of practical importance for innovative research fields (for example, electron bonding of clusters through vertical, synthesis of 3D lattices comprising islands-clusters often referred to as *artificial atoms* [56,57]).

4. Electrical and optical properties of 'artificial atom' systems

4.1. Few-hole ground states of charge-tunable self-assembled array of quantum dots

The above procedure has a great potential for electronic states studies and realization of some novel concepts of quantum-effect GeSi devices which require regular arrays of QDs. Band lineups at strained-layer interface for Ge on Si show a large valence band offset which offers hole zero-dimensional states in Ge QDs. The energy of a hole confined in a QD is strongly quantized and the energy spectrum is discrete. In typical structures with characteristic dimensions of 10 nm, the distance between neighboring energy levels is on the order of a few tens of meV.

The ground state of the electronic system in an atom is in the first place determined by quantization of the single-electron motion in the Coulomb field of the nucleus (spatial quantization). The characteristic energy of interactions between electrons in many-electron atoms is smaller than the spatial quantization energy. Since the dimensions of QDs are visible larger than those of atoms, the Coulomb interaction is of much greater significance [58]. The spatial quantization of energy depends on size L as $1/L^2$, while the Coulomb interaction energy behaves as $1/L$. The Coulomb repulsion favors pushing the electrons apart from one another, whereas the external confinement squeezes electrons in the center of the dot and prevents a large separation between them [58]. In present studies Ge 'hut'-clusters with the areal density 3×10^{11} cm^{-2} and the typical base length 12–15 nm have been grown at 300°C on p-type Si (001) substrate by MBE. The measurement of the quantum levels and Coulomb charging of self-assembled Ge QDs imbedded in Si barriers was made by using the capacitance [59] and admittance [60] spectroscopy, as well as with field-effect studies [61] in the structures which contain as many as 10^9 dots. Due to reduced inhomogeneous broadening one may observe the single-electron charging of the s and p shells in the capacitance and field-effect spectra of such self-assembled QDs. The Coulomb energy as a function of hole number per dot was found to be determined.

For a field-effect device the change in channel conductance with gate voltage is shown in Fig. 6. Conductance G increases at negative V_g as would be expected from the p-type nature of the material. Devices, which contain well-defined dots (8–13 ML of Ge), show the conductance oscillation with gate voltage. The distance between successive conductance peaks, ΔV_g, depends on the average Ge thickness, in particular ΔV_g decreases with increasing QD size. At high temperatures, the peak width widened and oscillations disappeared.

The oscillating component was attributed to conduction by hopping of holes between dots. Applying the gate potential induces a charge into the system. This results in filling of the dots by holes. Since the density of states in the QDs is

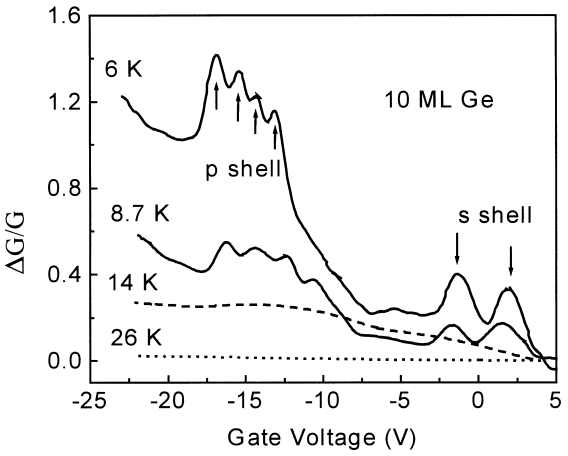

Fig. 6. Field effect for the 10 ML sample at various temperatures.

discrete, the change of dot occupation gives rise to distinct features in the G–V_g traces. The condition for a maximum in conductance is that the corresponding level is only half-filled. In the case of a fully occupied state, the hole has to be activated to the next energy level in a dot. This requires larger activation energy, and therefore the conductance associated with this process is smaller. Thus, the conductance spectrum reflects directly the hole energy spectrum in the QDs. A similar modulation of drain current has been observed by Horiguchi [62] in InAs QD field-effect structures using a split gate structure. Remarkably, in Ge–Si structures [63], well-resolved conductance oscillations are observed in channels which contain about 10^9 dots, whereas in the InAs–GaAs system there were only InAs dots between the split gate electrodes [62].

In a magnetic field, the field effect decreases corresponding to a positive magnetoresistance (MR) [61]. The most important finding is the rapid disappearance of the conductance oscillations. This is seen more clearly for exited states in QDs and less pronounced for the ground energy state. An exponentially large positive MR is a characteristic feature of hopping conduction. It arises from shrinkage of the wave functions in a direction transverse to the magnetic field orientation and is therefore very sensitive to the localization radius, l. The obvious difference between the behavior of the conductivity oscillations in a magnetic field for excited states and for the ground state results from the difference in their spatial dimensions. Estimation the relation between the characteristic lengths of excited l_e and ground states l_e has given $l_{ex}/l_{gr} \approx 3$ [61].

For the 8 ML and 10 ML samples, the conductance structure reveals two distinct shells of the hole states in the Ge QDs. The first shell contains two peaks, the second displays four well-pronounced maxima (Fig. 6). This structure can be explained well by the model, which assumes a two-dimensional parabolic lateral confinement in the dots [58]. At zero magnetic field, the energy-level diagram consists of equidistant states. The s-like ground state can accommodate only two holes. The p-like first excited state has a twofold orbital as well as twofold spin degeneracy. However, the degeneracy of the states is lifted by electron-electron interaction in the dots. So the difference in the gate voltage between loading of the $(N-1)$ and N holes into the same shell is a direct consequence of Coulomb repulsion. The energy level separation ΔE of the different charge states in the dots can be estimated by using $\Delta E = \eta e \Delta V_g$, where the gate modulation coefficient η relates the gate voltage to the hole energy inside the dot. For a given geometry, $\eta = 0.84 \times 10^{-2}$ [61]. The estimated energy gap between singly and doubly occupied states, the s–s correlation energy, E^{s-s}, is 28 meV. This value is in reasonable agreement with the charging energy obtained in the capacitance spectroscopy experiments [63], 36 meV, and by studies of the barrier admittance [64] 29 meV. Similarly, the charging energy of the p-states is calculated to be $E^{p-p} \approx 11$ meV. To our knowledge, this is the first determination of this quantity. Note that E^{p-p} is smaller than E^{s-s} by a factor of about three. The reason is that the spatial dimension of the wave function of the excited states is larger than that of the ground state. Therefore the interaction energy gets smaller. This explanation implies $l_p/l_s \approx 3$, which agrees well with analysis of the magnetoresistance data. Similar calculations of the characteristic energies were made for the other samples, in particular for the 8 ML and 13 ML and the results are depicted in Fig. 7. It seems to be quite reasonable that all energies decrease with increasing the nominal Ge thickness due to increase of the QD's size. The bare separation of the s and p energy levels in the dots, δ_{sp}, which does not include the interaction energy and represents the quantization energy, was found to be ≈86 meV, which is close to the value of about 80 meV observed in resonant tunneling experiments [65].

The dynamics of loading process of holes into the first excited state of Ge QDs was investigated with admittance spectroscopy [60]. The admittance spectra reveal four peaks which are attributed to the splitting of the p-like shell by electron-electron interaction. The activation energies are determined to be $E_1 = 201 \pm 7$ meV, $E_2 = 228 \pm 7$ meV,

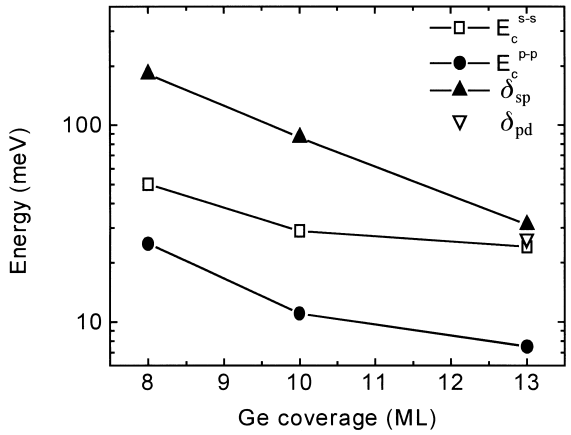

Fig. 7. Variation with Ge coverage of correlation (charging) energies in the s and p shells, E_c^{s-s} and E_c^{p-p}, and the bare level spacings, δ_{sp} and δ_{pd}.

$E_3 = 267 \pm 12$ meV, and $E_4 = 288 \pm 10$ meV. The level spacing between four states in the p-shell of about 20–30 meV seems to be quite reasonable and agrees well with the charging energy determined by Zhang [64] and with results of the transport measurements [61] in Ge QDs of the similar size. The hole capture cross sections of the quantum levels were found to be in the range from 10^{-12}–10^{-6} cm^{-2} with top value for deeper energy level.

4.2. Photoconductivity and luminescence.

Inter- and intraband optical transitions in semiconductor QDs are believed to be of practical interest for the development of a new generation of infrared photodetectors which should operate from near- to far-infrared. Since the density of states in QDs consists of discrete levels whose population can be easily monitored, the obvious advantage of the three-dimensionally confined systems is the possibility of tuning their photoresponse for the desirable spectral range. In contrast to two-dimensional systems, the lateral confinement of carriers in QDs and hence in-plane polarization of the transitions make excitation at normal incidence possible providing the large absorption quantum efficiency. Most of the works to date have concentrated on the InAs–GaAs heterosystem [66–69]. In particular, the intraband absorption due to transitions between confined holes and bound-to-continuum electronic transitions polarized along the growth axis have been investigated by photoinduced infrared spectroscopy. Sun et al. [69] have applied photovoltage and photoreflectance spectroscopy to study the interband excitonic transitions in the same system. Optical properties of Ge-on-Si self-assembled QDs are less studied despite they have an advantage due to possibility of integration with the silicon-based signal processing electronics. Abstreiter et al. [70] have found that Si pin diode with a stack of seven layers of Ge islands embedded in the intrinsic region exhibits significant photocurrent below the energy gap of Si with onset of absorption at 0.825 eV. Recent experiments with Ge–Si multilayer structures have demonstrated possibility of the inter- and intraband absorptions also in mid-infrared range [71,72]. Note the areal density of the Ge islands in these works was less than 10^{10} cm^{-2}.

The normal-incidence infrared photoconductivity was studied in silicon pin diode embedded with a single layer of Ge self-assembled QDs. The large areal density of Ge QDs (3×10^{11} cm^{-2}) allows to realize the high absorption coefficient in the QDs layer and observe reverse bias-tunable photoconductivity maxima at ≈430 meV (2.9 μm) and at ≈730 meV (1.7 μm). To the best of our knowledge, the experiment reported here is the first observation of mid-infrared photoconductivity in Ge QDs.

Fig. 8 depicts the measured photoconductivity spectral response of the QD's sample as a function of reverse bias. There are apparent two photoconductivity peaks below the silicon interband absorption edge which are changed with the applied voltage in a different way. The response from the

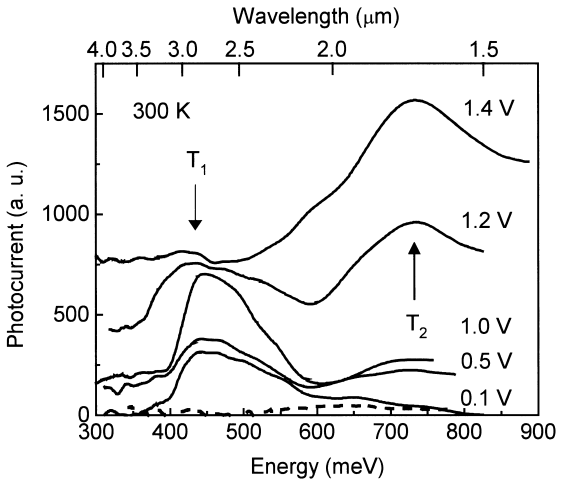

Fig. 8. Photocurrent spectra at 300 K as a function of reverse bias. The curves have been offset vertically for clarity. Dash line demonstrates the disappearance of the response for a sample without quantum dots (only 5 ML Ge wetting layer was grown).

5 ML sample (dashed line) does not display any features in the investigated energy range. Therefore, we may argue that the observed PC signal is due to carrier transitions out of the dots. We have demonstrated Ge QD infrared photodetector whose spectral response is in-plane polarized and consists of two peaks. The mid-infrared absorption around 2.9 μm is attributed to the intraband hole bound-to-continuum absorption, while the near-infrared photocurrent maximum (1.7 μm wavelength) is probably due to the interband excitonic transition. The conclusion we may draw from the data is that by application the reverse bias we can tune the device for the near- or mid-infrared response.

4.3. Stacked arrays of Ge quantum dots

We also synthesized multilayer structures comprising ten layers of QDs (Fig. 9). They were synthesized using a Katun MBS installation. Ten Ge layers of 1.4 nm thickness were grown at the rate of 0.03 nm/s at the substrate temperature 300°C. They are separated from one another by 10 nm Si layers. The average size of bases of 'hut'-clusters, and their density were 15 nm and 3×10^{11} cm^{-2}, correspondingly. These data were supported by ex situ STM studies. The high density of QDs at low size dispersion (less than 20%) determines their uniform electrical and optical characteristics. Photoluminescence spectra recorded for these structures by three independent research teams (Fig. 10) argue a high level of ordering of these nanoobjects (Liu and Lagally [15]).

5. Conclusions

Current status of the research in the field of synthesis and application of silicon and germanium-based nanostructures were reviewed in the present paper. The problem was found

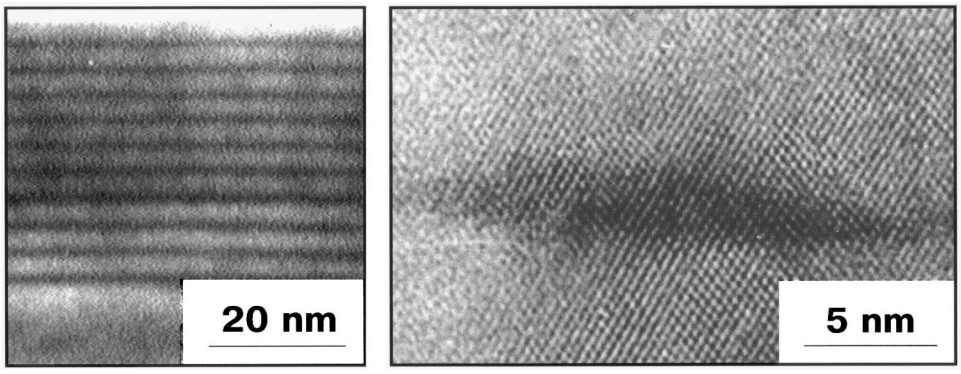

Fig. 9. The XTEM cross section of the ten sheets of Ge dots in Si matrix and its fragment with Ge cluster. Performed by A.K. Gutakovsky (ISP SB RAS).

to be of increased interest to scientists and technologists: number of publications under consideration increases up to now. There was an obvious conclusion on the importance of mechanical strains and their elastic relaxation in the processes of nanostructure self-organization which makes crucial changes to the classical set of phase-formation mechanisms. Various types of ordering were classified in the nanocluster systems under consideration: in cluster shape, in its size, in distance between islands, as well as ordering through vertical, i.e. in successively growing multilayer structures containing QDs. Methods for enhancing the ordering level of nanostructures involving QD arrays and for attaining their minimal size at large density of their distribution through the surface are discussed.

Capacitance and admittance spectroscopy studies and field-effect measurements in the structures which contain as many as 10^9 Ge dots enable to resolve well-pronounced peaks attributed to single-electron charging of each dot with up to six holes. The energy level structure reveals up to three distinct shells which interpreted as the *s*-like ground state, first excited *p*-like state and second excited *d*-like state. The hole correlation (charging) energies, the quantization energies, localization lengths, hole emission time constants associated with the quantum levels in the dots were determined. Ge QD infrared photodetector was found to consist of two bias controlled peaks in mid-infrared region.

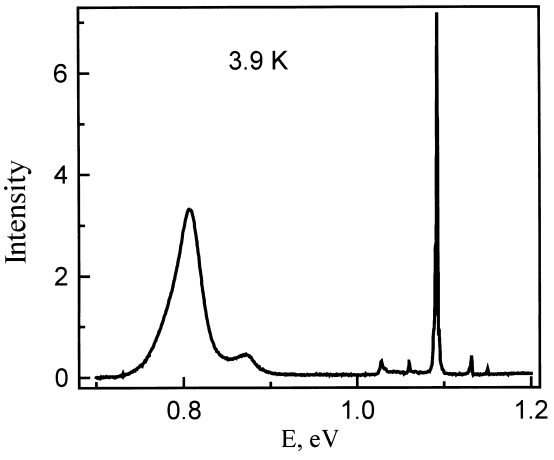

Fig. 10. Photoluminescence spectrum from the Ge quantum dot array shown in Fig. 9. Measurements performed by M. Goryll (ISI, Jülich).

Acknowledgements

The research was supported by the Russian Foundation for Basic Research (Grants 97-18408, 97-18409 and 99-02-17019) as well as by Programs of the Ministry of Science and Technology of the Russian Federation 'Physics of Solid Nanostructures' (Project 97-2025) and 'Promising Technologies and Devices of Micro and Nanoelectronics' (Project 02.04.1.1.16.E.1).

References

[1] R.A. Mezger, Semicond. Comp. 1 (1995) 21.
[2] U. Konig, Phys. Scripta T68 (1996) 90.
[3] R.A. Soref, Thin Solid Films 294 (1997) 325.
[4] T. Tashiro, T. Tatsumi, M. Sugiyama, T. Hashimoto, T. Morikawa, IEEE Trans. Electron. Devices 44 (1997) 545.
[5] D.J. Paul, Thin Solid Films 321 (1998) 172.
[6] D. Leonard, M. Krishnamurthy, C.M. Reaves, S.P. Denbaars, P.M. Petroff, Appl. Phys. Lett. 63 (1993) 3203.
[7] D. Leonard, K. Pond, P.M. Petroff, Phys. Rev. B 50 (1994) 11687.
[8] J.-M. Marzin, J.-M. Gerard, A. Izrael, D. Barrier, Phys. Rev. Lett. 73 (1994) 716.
[9] A.I. Yakimov, V.A. Markov, A.V. Dvurechenskii, O.P. Pchelyakov, Philos. Mag. B 65 (1992) 701.
[10] L.N. Aleksandrov, R.N. Lovyagin, O.P. Pchelyakov, S.I. Stenin, J. Cryst. Growth 24/25 (1974) 298.
[11] O.P. Pchelyakov, V.A. Markov, A.I. Nikiforov, L.V. Sokolov, Thin Solid Films 306 (1997) 299.
[12] D.J. Eaglesham, M. Cerullo, Phys. Rev. Lett. 64 (1990) 1943.
[13] S. Guha, A. Madhukar, K.C. Rajkumar, Appl. Phys. Lett. 57 (1990) 2110.
[14] R. Nötzel, Semicond. Sci. Technol. 11 (1996) 1365.
[15] F. Liu, M.G. Lagally, Surf. Sci. 386 (1997) 169.
[16] N.N. Ledentsov, V.M. Ustinov, V.A. Shchukin, P.S. Kop'ev, Zh.I. Alferov, D. Bimberg, Semiconductors 32 (1998) 343.
[17] P. Müller, R. Kern, J. Cryst. Growth 193 (1998) 257.
[18] A.A. Chernov, in: D.T.J. Hurle (Ed.), Handbook of Crystal Growth, Vol. 3, North-Holland Elsevier, Amsterdam, 1994 p. 1086.
[19] F. Liu, M.G. Lagally, Phys. Rev. Lett. 76 (1996) 3156.

[20] R.J. Asaro, W.A. Tiller, Metall. Trans. 3 (1972) 789.
[21] M.A. Grinfeld, Sov. Phys. Dokl. 31 (1986) 831.
[22] W. Dorsch, H.P. Strunk, H. Wawra, G. Wagner, J. Groenen, R. Carles, Appl. Phys. Lett. 72 (1998) 179.
[23] Yu.B. Bolkhovityanov, V.I. Yudaev, A.K. Gutakovsky, Thin Solid Films 137 (1986) 111.
[24] S.A. Kukushkin, A.V. Osipov, Physics-Uspekhi 41 (1998) 983.
[25] I.M. Lifshitz, V.V. Slyozov, J. Phys. Chem. Solids 19 (1961) 35.
[26] B.K. Chakraverty, J. Phys. Chem. Solids 28 (1967) 2401.
[27] M.C. Bartlet, J.W. Evans, Phys. Rev. B 46 (1992) 12675.
[28] N.C. Bartelt, W. Theis, R.M. Tromp, Phys. Rev. B 54 (1996) 11741.
[29] I. Goldfarb, P.T. Hayden, J.H.G. Owen, G.A.D. Briggs, Phys. Rev. B 56 (1997) 10459.
[30] S. Lee, I. Daruka, C.S. Kim, A.-L. Barabasi, J.L. Merz, J.K. Furdyna, Phys. Rev. Lett. 81 (1998) 3479.
[31] T.I. Kamins, G. Medeiros-Ribeiro, D.A.A. Ohlberg, R. Stanley Williams, J. Appl. Phys. 85 (1999) 1159.
[32] A.R. Avery, H.T. Dobbs, D.M. Holmes, B.A. Joyce, D.D. Vvedensky, Phys. Rev. Lett. 79 (1997) 3938.
[33] J. Drucker, Phys. Rev. B 48 (1993) 18203.
[34] Y. Chen, J. Washburn, Phys. Rev. Lett. 77 (1996) 4046.
[35] D.E. Jesson, G. Chen, K.M. Chen, S.J. Pennycook, Phys. Rev. Lett. 80 (1998) 5156.
[36] M. Kästner, B. Voigtländer, Phys. Rev. Lett. 82 (1999) 2745.
[37] T.I. Kamins, E.C. Carr, R.S. Williams, S.J. Rosner, J. Appl. Phys. 81 (1997) 211.
[38] G. Medeiros-Ribeiro, A. Bratkovski, T. Kamins, D. Ohlberg, R. Williams, Science 279 (1998) 353.
[39] G. Medeiros-Ribeiro, T.I. Kamins, D.A.A. Ohlberg, R.S. Williams, Phys. Rev. B 58 (1998) 3533.
[40] T.I. Kamins, G. Medeiros-Ribeiro, D.A.A. Ohlberg, R.S. Williams, Appl. Phys. A 67 (1998) 727.
[41] R. Williams, G. Medeiros-Ribeiro, T. Kamins, D.A. Ohlberg, J. Phys. Chem. B 102 (1998) 9605.
[42] T.I. Kamins, G.A.D. Briggs, R.S. Williams, Appl. Phys. Lett. 73 (1998) 1862.
[43] F.M. Ross, J. Tersoff, R.M. Tromp, Phys. Rev. Lett. 80 (1998) 984.
[44] V.A. Shchukin, D. Bimberg, Appl. Phys. A 67 (1998) 687.
[45] P. Müller, R. Kern, J. Cryst. Growth 193 (1998) 257.
[46] Y.-W. Mo, D.E. Savage, B.S. Swartzentruber, M.G. Lagally, Phys. Rev. Lett. 65 (1990) 1020.
[47] S.M. Pintus, S.M. Stenin, A.I. Toropov, E.M. Trukhanov, V.Yu. Karasyov, Thin Solid Films 151 (1987) 275.
[48] J.A. Floro, E. Chason, L.B. Freund, R.D. Twesten, R.Q. Hwang, G.A. Lucadamo, Phys. Rev. B 59 (1999) 1990.
[49] V.A. Markov, A.I. Nikiforov, O.P. Pchelyakov, J. Cryst. Growth 175/176 (1997) 736.
[50] Z. Jiang, H. Zhu, F. Lu, et al., Thin Solid Films 321 (1998) 60.
[51] V.A. Markov, O.P. Pchelyakov, L.V. Sokolov, S.I. Stenin, S. Stoyanov, Surf. Sci. 250 (1991) 229.
[52] Y. Kim, B.D. Min, E.K. Kim, J. Appl. Phys. 85 (1999) 2140.
[53] J. Zhu, K. Brunnerand, G. Abstreiter, Appl. Phys. Lett. 73 (1998) 620.
[54] O.P. Pchelyakov, I.G. Neisvestnyi, Z.Sh. Yanovitskaya, Phys. Low-Dim. Struct. 10/11 (1995) 389.
[55] H. Omi, T. Ogino, Appl. Surf. Sci. 130–132 (1998) 781.
[56] G. Springholz, V. Holy, M. Pinczolits, G. Bauer, Science 282 (1998) 734.
[57] Y.W. Zhang, S.J. Xu, C.-H. Chiu, Appl. Phys. Lett. 74 (1999) 1809.
[58] L. Jacak, P. Hawrylak, A. Wojs, Quantum Dots, Springer, Berlin, 1998.
[59] A.I. Yakimov, A.V. Dvurechenskii, A.I. Nikiforov, O.P. Pchelyakov, Thin Solid Films 336 (1998) 332.
[60] A.I. Yakimov, A.V. Dvurechenskii, A.I. Nikiforov, O.P. Pchelyakov, Phys. Low-Dim. Struct. 3/4 (1999) 99.
[61] A.I. Yakimov, C.J. Adkins, R. Boucher, A.V. Dvurechenskii, A.I. Nikiforov, O.P. Pchelyakov, Phys. Rev. B 59 (1999) 12598.
[62] N. Horiguchi, T. Futatsugi, Y. Nakata, N. Yokoyama, Appl. Phys. Lett. 70 (1997) 2294.
[63] A.I. Yakimov, A.V. Dvurechenskii, A.I. Nikiforov, O.P. Pchelyakov, Lett. 68 (1998) 135.
[64] K. Zhang, H.J. Zhu, F. Lu, Z.M. Jiang, X. Wang, Phys. Rev. Lett. 80 (1998) 3340.
[65] A.I. Yakimov, A.V. Dvurechenskii, A.I. Nikiforov, O.P. Pchelyakov, J. Phys. Condens. Matter 6 (1994) 2573.
[66] S. Sauvage, P. Boucaud, F.H. Julien, J.-M. Gerard, V. Thierry-Mieg, Appl. Phys. Lett. 71 (1997) 2785.
[67] S. Sauvage, P. Boucaud, F.H. Julien, J.-M. Gerard, J.-Y. Marzin, J. Appl. Phys. 82 (1997) 3396.
[68] S. Sauvage, P. Boucaud, F.H. J, M. Gerard, V. Thierry-Mieg, J. Appl. Phys. 84 (1998) 4356.
[69] B.Q. Sun, Z.D. Lu, D.S. Jiang, et al., Appl. Phys. Lett. 73 (1998) 2657.
[70] G. Abstreiter, P. Schittenhelm, C. Engel, E. Silveira, A. Zrenner, D. Meertens, W. Jager, Semicond. Sci. Technol. 11 (1996) 1521.
[71] J.L. Liu, W.G. Wu, A. Balandin, G.L. Jin, K.L. Wang, Appl. Phys. Lett. 74 (1999) 185.
[72] P. Boucaud, V. Le Thanh, S. Sauvage, D. Debarre, D. Bouchier, Appl. Phys. Lett. 74 (1999) 401.