Investigation and Control of the Surface Processes During Semiconductor Nanostructures Formation by MBE*

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Epitaxial growth mechanism of Ge and Si thin films and nanostructures, including superlattices, quantum wells and quantum dots, are studied by means of reflection high energy electron diffraction (RHEED) and ellipsometry. The new capabilities to investigate and manipulate sufarce processes during molecular beam epitaxy (MBE) with synchronization of nucleation on atomic scale using impulsive outside actions are discussed.

I. Introduction

Recently the surface of the Ge/Si semiconductor heterostructure has received a great deal of attention. It has become tlie subject of iiitensive study.

Ge films grown on Si (111) 7 × 7 substrate surfaces have been studied early by nondestructive methods in the MBE, process[1–3]. It has been found that the growth mode of Ge films 011 Si (111) 7 × 7 is of the Stranski-Krastanov type and tlie critical film thickness of two-dimensional (2D) layers is about h=2.5nm. At this thickness *a* break in tlie pseudomorphic film growth is arcompanied by tlie emergence of flat islands containing misfit dislocations. As is generally known, the iiicrease in the interface eiiergy caused by the formation of misfit dislocations could be a reason for the transiticn from the 2D growth mode to the three-dimensional (3D) nucleation mode. The dislocation structure of Ge films on the Si (111) face has been thoroughly investigated[1,2]. A detailed analysis of the reasons for tlie formation of various superstructures as well as of the conditions of superstructure transition in the Ge/Sii(111) and $Ge_xSi_{1-x}/Si(111)$ systems has been made in our paper based on both the in-house research data and the data obtained by other investigators[3]. Depending on the film thickness and growth conditions the Si(111)(7x7), Ge(111)(5x5), Ge(111)(7x7)Si and Ge(111)c(2x8) supertructures were observed on the surface of epitaxial Ge films and GexSil-x solid solution. When the effective Ge film thickness does not exceed 0.2 nm, the Ge adsorption on the Si(111)(7x7) surface leads to stabilization of the (7x7) superstructure. As a result, the temperature of the reversible (7 x 7) → (1×1) transitions rises up to 950°C. At the stage of pseudomorphic growth, when the film and substrate lattice parameters in the surface coincide, the compressive stresses affecting the film induce the appearance of the Ge(111)(5x5) superstructure. This superstructure is stable within the range of elastic deformation from 0.6 to 4%.

The plastic relaxation of the strains that occurs with. increasing Ge film thickness is accompanied by the irreversible Ge(111)(5x5)→Ge(111)c(2x8) at $T_s < 450$°C or by the irreversible Ge(111)(5x5)→Ge(111)(7x7) transition at T > 450°C.

The Ge(111)(7x7)Si superstructure is induced by tlie presence of Si atoms on the film surface due to, diffusion and, probably, by surface segregation of Si at T > 450°C. The temperature of the reversible Ge(111)(7x7)Si→Ge(111)(1x1) transition rises with increasing T_s which is connected with the increase of the amount of the Si atoms on the surface layer of the film.

*Invited talk.

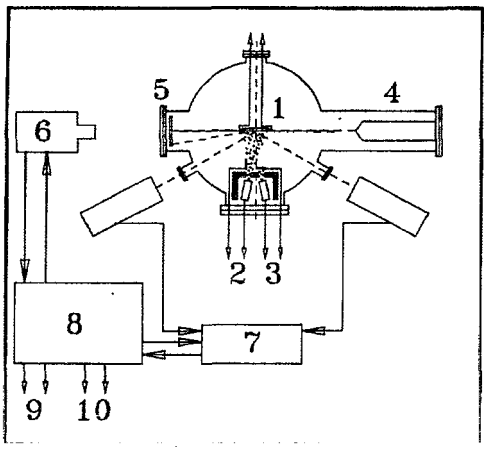

Figure 1: Schematic drawing of tlie MBE system. (1. Sbstrate; 2,3. MBE sources; 4. RHEED gun; 5. RI-IEED screan; 6. Video system; 7. Ellipsometer; 8. Personal computer; 9,10 Control output.)

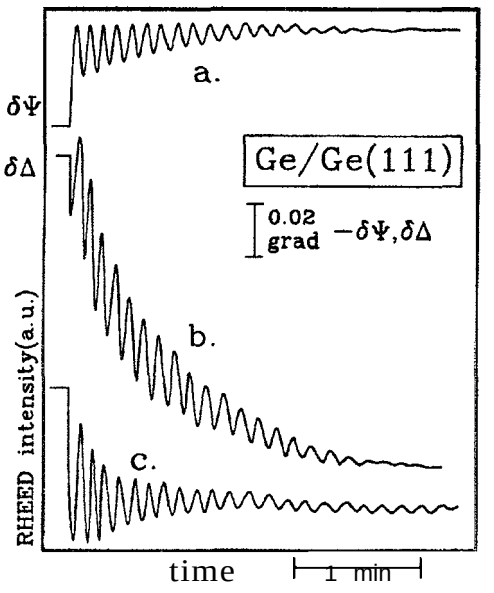

Figure 2: Dependences of ellipsometric angles Ψ (a): **A** (b) and RHEED specular beam intensity (c) on time of Ge film growth (T=380°C).

On tlie basis of these iiivestigations, a.phase diagram of the surface structure during molecular beam epitaxy (MBE) of Ge on an Si substrate has been made using reflection high energy electron diffraction (RIIEED).

In contrast to RIIEED tlie automatic laser ellipsoinetry (ALE) is not so widely used by tlie MBE technique. This paper reviews some of the results of the combined application of RHEED and ALE as nondestructive methods for investigation and control of the morphology, thickness, structure and optical characteristics of thin epitaxial films, superlattices and their surface layers "in situ" during MBE.

II. Experimental

Tlie experiments are carried out on a home made MBE system, fitted with an electron gun for RHEED, ALE with wavelength of 632.8nm, a.mass spectrometer and an Auger-spectrometer (Fig. 1).

The Ge substrate was prepared by growing and annealing a 200 nm thick Ge buffer on Si(111) at T_s = 450°C. The investigations of initial growtli stages of Ge on Ge(111) was performed at a substrate temperature above that of the c(2x8) - (2x2) phase transition (240-300°C) with a glowth rate of about four monolayers per minute[1−4]. RHEED (40 kV) intensity oscillations of the specular beam were measured by a photometer with a photomultiplier as a detector. The incident angle was 2.2°, corresponding approximately to destructive interference for the stepped surface. Our results suggest that the definition of particular point in the growth sequeiice by using RHEED intensity oscillations requires very specific diffraction and intensity registration conditions.

Before each experiment on observation of oscillations we carry out an annealing at the temperature of T_s = 450°C about 10 min in order to restore the original morphological, structural and optical properties of the surface. During the the growth we measure tlie perioclicai changes in specular electron beam intensity and in the ellipsometric angle A and Ψ (Fig.2)[5]. An increase in the growth rate due to an increase in temperature shortens tlie oscillation period hoth in A and Ψ [3]. The change in the filin thickness per period of the oscillations in A and Ψ is equal to the germanium lattice constant ±1.5%. This data can be used to evaluate tlie sublimation enthelpy of Ge.

The damping of the oscillations which is evident on tlie curves apparently results from a relaxation to a steady - state relief in the cause of the growth process. Tlie both type oscillations were disappeared under in-

crease of substrate temperature. Under tliese conditions tlie mode of growth changes from 2D islands to step-flow mcde. For every temperature there exists a critical substrate temperature at which oscillations disappear. This effect can be used to evaluate the activiation eiiergy of surface migration of Ge atoins.

Tlie complete matching of conditions under which tlie oscillations in the ellipsometric angles and tlie electron specular beam intensity are observed is tlie <:vidence that these phenomena have a common origiii.

An impo:tant result of these experiments, consequently, is tl e conclusioii that tlie phenomenon of oscillations of c ptical characteristics of the surface can be utilized to st idy growtli processes specially under conditions when RHEED cannot be used. It is important for example if tlie material undergoes changes during bombardment by the electron beam or if the process is carried out in a medium which is dense for an electron beam[6].

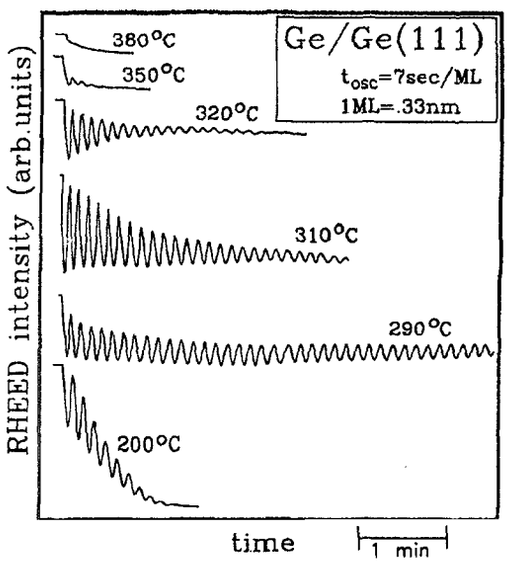

Figure 3: RHEED oscillatioiis during Ge films growth at various substrate temperatures.

III. On tlie origiii of RHEED oscillations dampiiig

The RHEED oscillations behavior depend drastically on growth temperature. That is reflected a.s in the essential variations of oscillations forms, so in both oscillations amplitude and damping time (Fig. 3).

Tlie dependence of the oscillation damping time on substrate tem perature T_s is shown at Fig. 4 for two Ge growth rates. This values has been obtained in a simple exponential approximation. The dependence oscillation damping time from T_s has a maximum at about 300°C. Similar temperature dependence of amplitude oscillations with maximum is observed (Fig. 4). We propose a change of oscillations damping mechanism near tlie temperature ($T_{\max}$) of maximal oscillations damping time ($\tau_{\max}$).

Bellow T_{max} damping occurs due to so called thickning of growth front. This mechanism is widely discussed in literature[1,2,7,8] and lead to the transformation of

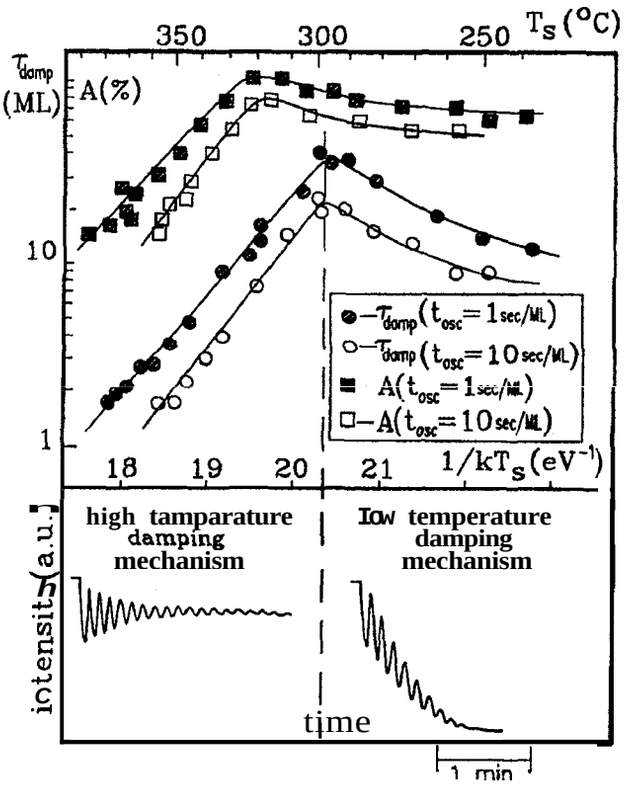

Figure 4: Dependeiices of oscillation damping time (open circle - t_{osc} = 10sec/ML; filled circles - t_{osc} = 1sec/ML) and amplitude (open squares - t_{osc} = 10sec/ML; filled squares - t_{osc} = 1sec/ML) *on* growth temperature.

a two-level surface wliich cbaracterizes an ideal two-dimensional growth mechanism into a multilevel one (Fig.5a). This effect is realized at a high nucleation rate as a result of the formation of new 2D nuclei on the surface of large 2D islands, placed on the second level, before complete filling of this level with atoms.

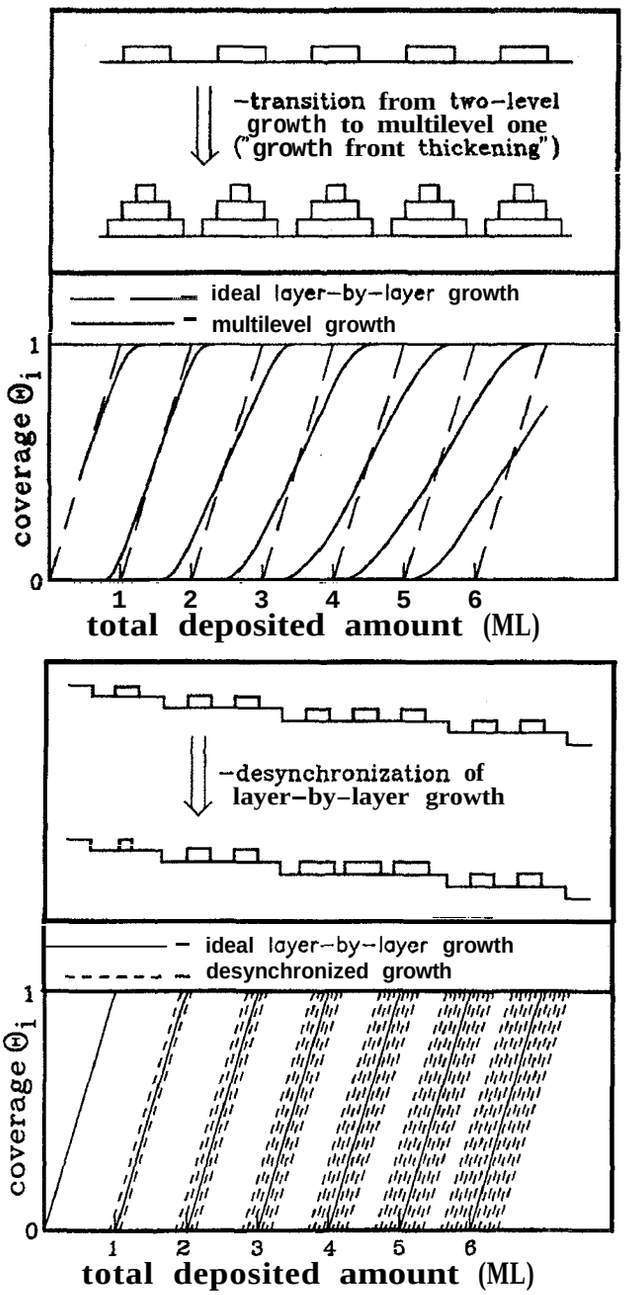

Figure 5: Schematical presentation of growth front thichning (a) and oscillations phase desynchronization (b) and correspondiiig first monolayers growth.

On the other hand, tlie increasing of 2D-nucleation time will bc observed with increasing of growth temperature. Fluctuations of this time is an increasing function of growth temperature also from common fluctuation theory. Deviations of the average nucleation time can increase since tlie existence of a notable variance in the width of terraces between monoatomic steps exists too. Thus oiie can expect that the appearance of 2D-nuclei on different terraces is not simultaneous (Fig.5b). Nucleation desynchronization will be most appreciable near the transition from the 2D mehanism to the step flow mechanism. In the same conditions the waiting time for nuclei formation can become a notable part of the oscillation period. As a result a phase shift, increasing with time, will appear between periodic processes of 2D nucleation and lateral growth up to their coalescence, occurring on the terraces of different width. Influente of such shift is schematically shown on Fig.5b. This will lead to coexistence of terraces with different stages of filling of the next monolayer at the stationary growtli regime and corresponding oscillation damping.

The RHEED-intensity after oscillation damping in the high temperature region is equalt ot about average between maxima and minima oscillations before damping. That confirms the proposed damping mechanism due to desynchronization of nucleation and existence of terraces monolayer coverage from 0 to 1.

IV. Features of surface recovery during interface formation is superlattices

The analysis of **RHEED** oscillations is a very effective and widely used tool for control of growth rate and layer thickness during MBE growth of multilayered heterostructures. Typical **RHEED** oscillations during growth of strained layers superlattices consisting of 4 ML of Ge_xSi_{1-x} solid solution and 5 ML of Si is shown on Fig. 6. The layer thickness is obtained by simple calculation of tbe number of oscillations, each corresponding to tlie growth of one monolayer. It is necessary to note, that the oscillation period is related to growth rate, but not to molecular beam fluxe intensity, as it is measured hy other tecliniques (quartz resonators, mass-spectroscopy, etc). This fact is very important in the

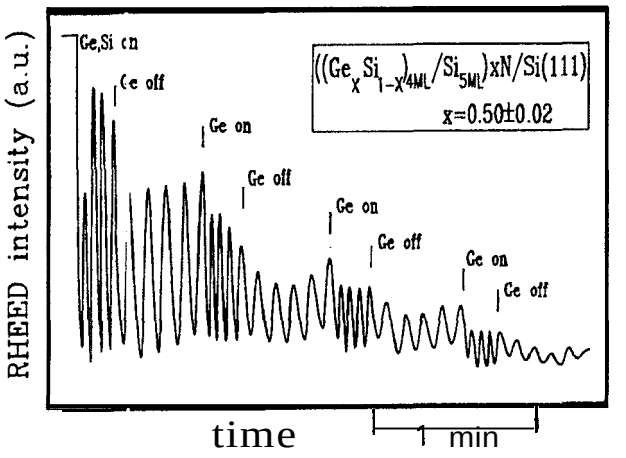

Figure 6: RIIEED oscillations during the MBE-growth of tlie Si - $Ge_{0.5}Si_{0.5}$ superlattice on Si(111).

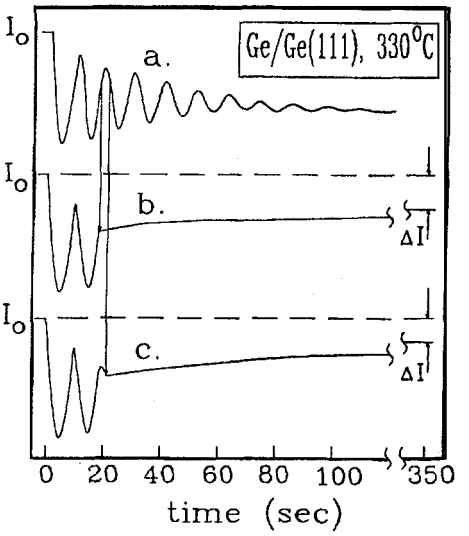

Figure 7: RHEED-intensity oscillation curves without. growth interruption **(a)** and with interruption before maximum (b) and after maximum (c).

case of essential film re-evaporation during growth or incomplete sticking.

Superlattice growth, shown on Fig. 6, was provided by opening of tlie Ge cell shutter after growth of 5 ML Si without closing of tlie Si cell shutter and by closing of the Ge cell after growth of 4 ML solid solution layer. Compositior of solid solution layer x is easily obtained from relation: $1 - X = t_2/t_1$ where t_2 and t_1 - are tlie periods of oscillation during growth of Si and Ge_xSi_{1-x} solid solution layers respectivcly.

Control of the phase of oscillations is very important for intcrface sharpness in atomic scale in MBE-produced multi-layered heterostructures. The sharpest surface is produced after growth termination at full monolayer coverage.

MBE grcwth with computer oscillation pliase control is called in literature Phase-Locked Epitaxy (PLE). This technicue is widely used for fabrication of superlattices and other multilayered semiconductor heterostructures from various materials[9,10]. Thus oscillation control is very important for successful MBE growth in many cases. Tbe quality of interfaces is a significant requirement for manufacture of semiconductor superlattices by MBE. The clesire to achieve an interface smoothness with a single-monolayer precision has prompted the development of growth processing techniques that utilize periodic interruptions in tlie incident molecular flux. The recovery processes, on the cessation of beam-flux are generally associated with growth front smoothing by thermodiffusion[11,12].

Layer completion dependencies of the surface recovery mode for Ge(111) films grown by MBE at substrate temperature $T_s = 350°C$ have been investigated through RHEED intensity recovery curve analysis. Experimental curves are given in Fig. 7. The recovery of tlie specular RHEED intensity $I(t)$ to initial pregrowth value has been fitted[13] by the expression

$$I(t) = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \ ,$$

mhere τ_1 and τ_2 are time constants for two recovery stage, because it reflects inigration processes which provide the final structure of the surface, and therefore pertains most directly to interface formation. Furthermore, a. nonsystematic trend has been found for τ_1. The characteristic recovery time τ_2, as a function of the point in the layer completion at which growth was terminated, is shown in Fig. 8a. Surface recovery is seen to occur most rapidly at interruption points of 0.1-0.3 layer completion.

In addition, we have employed computer Monte-Carlo simulation (with animation) to reveal the individual processes that are responsible for smoothing. Our approach is based on the solid-on-solid model: the substrate is described as a simple-cubic lattice with neither

volume vacancies nor overhangs. The simulation was was performed on a 32x32 lattice with periodic boundary conditions. Surface migration is modelled as an intersite hopping process with an Arhenius rate determined by the local nearest-neighboring environment. The recovery is monitored by measuring the surface step density, shown to provide qualitative agreement with RHEED measurements[14].

It is seen from direct observation, provided by computer animation, surface recovery results from migration of adatoms when the growth is terminated with less than a half layer completion. In contrast, recovery is due primary to surface vacancies when a layer is almost complete. In this case the recovery process is limited by the motion of isolated particles (atoms or vacancies) from surface clusters or depressions to terrace edges. We suggest that the diffusion hopping rates of adatoms and vacancies are different. For very different hopping probabilities of atoms and vacancies, surface recovery has been been found to be strongly dependent, on layer completion. In this way, the ratio of hopping probabilities of adatoms to that of vacancies has been estimated. It seems to be about four orders of magnitude.

Turning to the analysis of RHEED intensity recovery, the roughness of the surface, determined as the ratio I/I_0 (see Fig.7), has been considered for different points in the layer completion. Each data point has been obtained for the same recovery time (Fig. 8b). The roughness shows a minimum at 0.16 layer completion. Taking into account that the layer completion of about 0.16 yields the most rapid recovery (Fig. 8a), this point may be regarded as the best moment of growth termination.

V. Molecular beam epitaxy with nucleation synchronization

The effect of both factors (thickening of growth front and 2D-nucleation desynchronization) leading to the damping of RHEED oscillations can be significantly reduced. One can achieve this by variation of supersaturation synchronized with oscillation. At the moment of

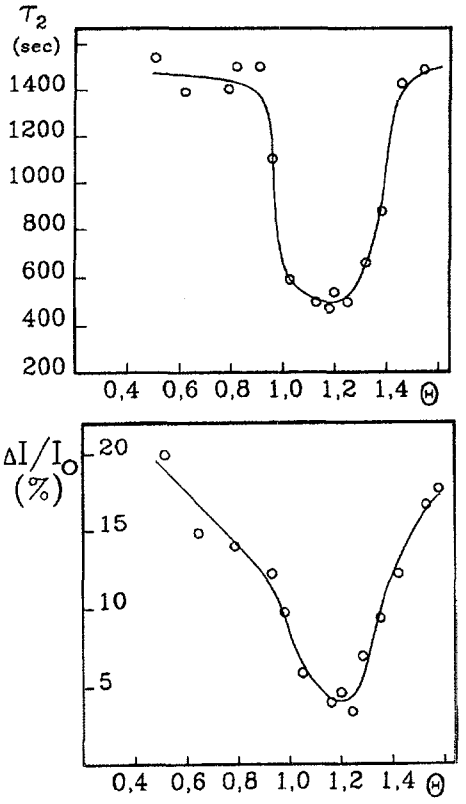

Figure 8: The layer-completion dependences of τ_2 (a) and I/I_0 (b).

appearance of the 2D-nuclei (stage 1) the supersaturation has to be higher than during their lateral growth and coalescence with formation of continuous monolayer (stage 2). In this case if supersaturation at the stage 1 is enough for formation of the 2D nuclei almost simultaneously on the all the terraces. It means that periodic variations of micro roughness on different terraces will always remain synchronous. At stage 2 supersaturation must be small enough to prevent the formation of new 2D-nuclei.

This way we report a technique to achieve sustained two-dimensional layer-by-layer Si and Ge growth by using periodic variation of supersaturation synchronized with RHEED oscillations. We call this technique *molecular beam epitaxy with nucleation synchronization (MBE-NS).*

The first test of MBE with nucleation synchronization was performed during homoepitaxy of elemental semiconductors: Ge and Si[15]. The Ge and Si fluxes were measured by the RHEED oscillations. to observed

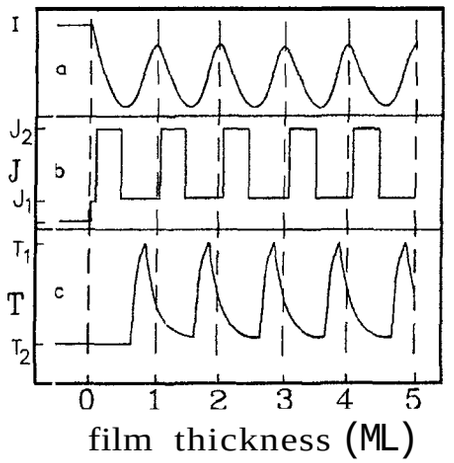

Figure 9: (a) - *RHEED* specular beam oscillation; (b) - molecular beam variation for nucleation synchronization (RIBE-NS-1); (c) - substrate temperature variation for nucleation synciironization (MBE-NS-2).

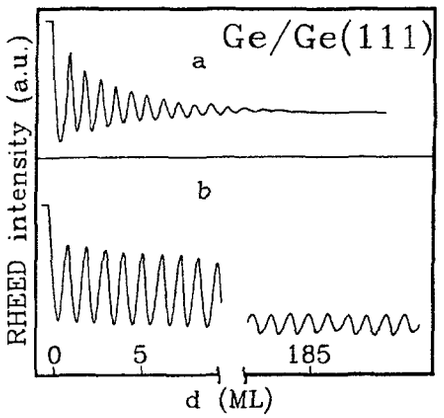

Figure 10: *RHEED* specular beam oscillation during the Ge film growth on Ge(111) at $T_s = 350°C$: (a) - without nucleation synchronization; (b) - with nucleation synchronization by flux variation (V1=0.03 nm/s, V2=0.1 nm/s).

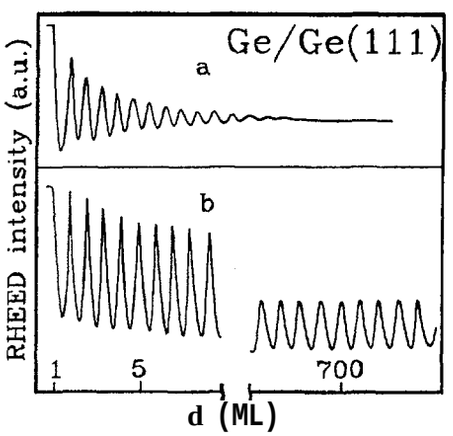

Figure 11: *RHEED* specular beam oscillation during the Ge film growth on Ge(111) substrates (V=0.03 nm/s): without nucleation synchronization (a); with nucleation synchronization by substrate teinperature variation ($T_{s1} = 330°C$, $T_{s2} = 345°C$) (b).

RHEED osc llations in the case of Ge growth, a 500 nm thick; buffer layer of Ge was annealed a.t 600°C to create the initial atomically smooth surface. Synchronization of the external perturbation changing supersaturation on the grow:h surface was perforined by a. computer in real time. The electrical signal corresponding to tlie specular beam intensity from tlie RHEED pattern was sent via an analog-digital converter to the control computer which determined the intensity maximum and minimum as function of time. The computer was also used to control the molecular-beam-cell shutter positions and the current sources heating the substrate.

Two modifications of tlie MBE-NS technique were realized:

1. Flux intensity variation was synchronized with oscillations (Fig.9a). This was achieved by the application of two cells at different temperatures (T_{c1} and T_{c2}) and with different operating time in tlie open state (Fig. 9b) at the constant substrate teinperature T_s.

2. Substrate temperature variation was synchronized with oscillations at the constant flux intensity (Fig.9c).

Fig.10 presents intensities (I) of specular reflection versus grow:h time for the usual MBE method (Fig. 10a) and tht: first modification of MBE-NS (Fig. 10b). From comparison of Fig. 10a. and Fig. 10b it follows that oscillation damping in the MBE-NS mode estimated by the relaxation time of the oscillation amplitude decreased hy a factor of 30. However, after 50 periods, the subsequent dainping is not ineasured.

Cyclic variation of T_s near the chosen value in the second modification of MBE-NS was carried out over a 50°C range. The beginning of the T_s increase coincided in time with the minimum of $I(t)$. The interrelation between the $I(t)$ dependence (a) and T_s variations (b) during tlie growth is shown in Fig. 9.

The RHEED oscillations for growth using the second modification of MBE-NS are shown in Fig.11 and 12. Tlie cyclic variation of T_s during the growth was synchronized with the oscillation as shown in Fig. 9c.

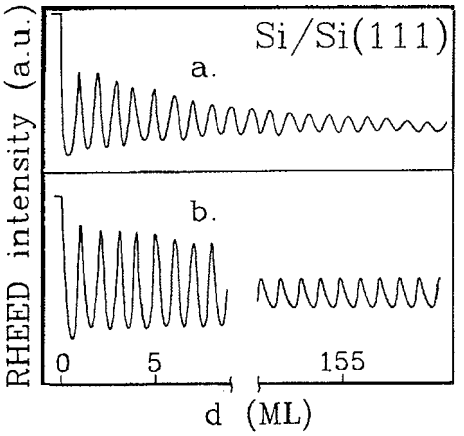

Figure 12: RHEED specular beam oscillation during the Si film growth on Si(111) at (V=0.03 nm/s): (a)- without synchronization; (b) - with nucleation synchronization by substrate temperature variation ($T_{s1} = 650°C$, ($T_{s2} = 690°C$).

In case of Ge growth (Fig.11) the temperature rise time after each oscillation minimum was 0.15 of tlie oscillation period, whereas for for Si epitaxy (Fig. 12) its value mas 0.25 of tlie period. Oscillation damping in tlie second modification of MBE-NS (Figures 11b and 1211) also decreased sharply compared with usual MBE (Figures 11a and 12a). In Fig. 11 the increase of tlie damping time was 100-folcl, aiid in Fig. 12 it was tenfold. In both figures 1111 and 12b a marked decrease of tlie oscillation amplitude is also observed during tlie first 30-50 periods, although subsequent variations of the amplitude were not observed.

In our opinion, MBE-NS modification can be used for growth not only of Ge and Si, but also 111-V, 11-VI materials. Creation of high supersaturation at tlie niooment of monolayer formation can be accomplished by techniques other than tlie two experimentally verified in this paper (for example, impulse laser evaporation).

The effect of tlie cliange in tlie layer-by-layer mode of growth to a three-dimensional mechanism a.t the moinent of strain relaxation ill tlie Ge-Si films at a critical thiclíness is investigated. This effect mas used to obtain Ge-droplets naiiostructures. Ge-islands are located in tlie plane between tlie two potential barriers formed by the Si layer ahout 10 nm thick. Periodic conductance oscillations on the nanostructures were observed[16].

VI. Summary

The following conclusions are confirmed by analysis of the periodical processes of 2D-nucleation and monolayer formation by 2D-islands coalescence during MBE, as well as recovery smoothing of the thin surface layer after growth stopping.

The comparison between tlie Monte-Carlo simulation and tlie experimental data on the diffusion smoothing of the growth surface suggests that the adatom mobility exceeds tlie surface vacancies mobility by four orders of magnitude. This allows to choose tlie optiinal moment of growth stopping between each layer in the superlattices. In our case it coniprises 0.1-0.3 completing of tlie monolayer.

We have found the new possibility to control atomic layer nucleation by the impulsive outside actions (temperature or intensity of molecular beam). By these means we can periodically increase the surface supersaturation synchronized with the completing of each atomic layer of thin films. A new MBE technique based on this possibility (MBE with synchronization of nucleation) (MBE-NS) is being devised.

Epistructures of any thickness can be grown with tlie MBE-NS. It can be usefully employed both to elementary seniiconcluctors and compounds (11-VI, 111-V etc.) in contrast to the atomic layer epitaxy technique (oiily for compounds). MBE-NS is also more effective then tlie pliase-loclíed-epitaxy technique, because it does not need interruptions for smoothing interfaces.

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